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## Shear banding in time-dependent flows of polymers and wormlike micelles

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# Shear banding in time-dependent flows of polymers and wormlike micelles

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## Synopsis

We study theoretically the formation of shear bands in time-dependent flows of polymeric and wormlike micellar surfactant fluids, focussing on the protocols of step shear stress, step shear strain (or in practice a rapid strain ramp), and shear startup, which are commonly studied experimentally. For each protocol we perform a linear stability analysis to provide a fluid-universal criterion for the onset of shear banding, following our recent letter [Moorcroft and Fielding, *Phys. Rev. Lett.* **110**, 086001 (2013)]. In each case this criterion depends only on the shape of the experimentally measured rheological response function for that protocol, independent of the constitutive properties of the material in question (Therefore our criteria in fact concern all complex fluids and not just the polymeric ones of interest here.). An important prediction is that pronounced banding can arise transiently in each of these protocols, even in fluids for which the underlying constitutive curve of stress as a function of strain-rate is monotonic and a steadily flowing state is accordingly unbanded. For each protocol we provide numerical results in the *rolie-poly* and Giesekus models that support our predictions. We comment on the ability of the *rolie-poly* model to capture the observed experimental phenomenology and on the failure of the Giesekus model. © 2014 The Society of Rheology. [<http://dx.doi.org/10.1122/1.4842155>]

## I. INTRODUCTION

Many complex fluids show shear banding, in which an initially homogeneous shear flow undergoes an instability leading to the formation of macroscopic bands of differing viscosity, which coexist at a common shear stress [Ovarlez *et al.* (2009); Manneville (2008); Olmsted (2008); Fielding (2007)]. Examples include entangled polymer solutions and melts [Ravindranath *et al.* (2008); Tapadia and Wang (2006); Boukany and Wang (2009a, 2009c)], triblock copolymer solutions [Berret and S  r  ro (2001); Manneville *et al.* (2007)], wormlike micellar surfactant solutions [Lerouge and Berret (2010); Boukany and Wang (2008); Helgeson *et al.* (2009a, 2009b); Hu *et al.* (2008); Miller and Rothstein (2007); Salmon *et al.* (2003a); Mair and Callaghan (1996, 1997); Makhloufi *et al.* (1995)], lyotropic lamellar surfactant phases [Salmon *et al.* (2003b)], concentrated suspensions and emulsions [Coussot *et al.* (2002); Paredes *et al.* (2011)], carbopol microgels [Divoux *et al.* (2010)], star polymers [Rogers *et al.* (2008)], and foams [Rodts *et al.* (2005)].

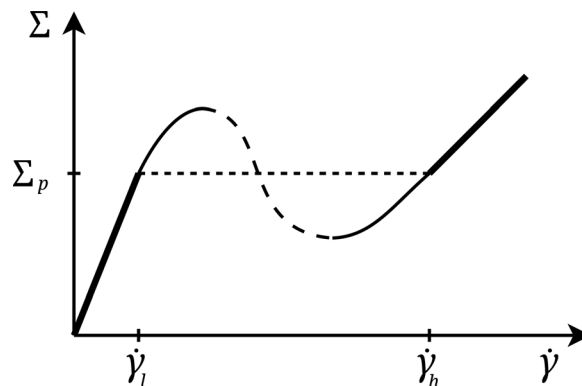
To date, most studies have focused on the long-time rheological response of these fluids once a steady flowing state has been established. The criterion for shear banding in this steady state limit is well known [Yerushalmi *et al.* (1970)]: that there exists a region

of negative slope in the constitutive curve of shear stress as a function of shear rate for an underlying base state of stationary homogeneous flow (In fact more recently constitutive models that couple strain and stress to auxiliary variables such as concentration [Fielding and Olmsted (2003b); Cromer *et al.* (2013)] or wormlike micellar length [Fielding and Olmsted (2004); Aradian and Cates (2005)] have been shown to display permanent banding even in regions of positive constitutive slope.). The steady state flow curve relation between stress and strain-rate then exhibits a characteristic plateau in the shear banding regime, signifying a coexistence of bands of differing shear rates  $\dot{\gamma}_l, \dot{\gamma}_h$  at a common value  $\Sigma_p$  of the shear stress (see Fig. 1).

However most practical flows involve a strong time-dependence, whether perpetually or during the initial startup of deformation before a steadily flowing state has been established. Accordingly, increasing experimental attention is now being devoted to time-dependent flow protocols. Shear banding has recently been reported following the imposition of a step stress [Gibaud *et al.* (2010); Divoux *et al.* (2011b); Boukany and Wang (2009a); Hu *et al.* (2007); Tapadia and Wang (2003); Hu *et al.* (2008); Boukany and Wang (2008); Hu and Lips (2005); Hu (2010)], following a step shear strain [Li and Wang (2010); Boukany and Wang (2009b); Wang *et al.* (2006); Fang *et al.* (2011); Ravindranath and Wang (2007); Archer *et al.* (1995); Boukany and Wang (2008)], and during shear startup [Divoux *et al.* (2010, 2011a); Boukany and Wang (2009a); Hu *et al.* (2007); Ravindranath *et al.* (2008); Martin and Hu (2012)].

In each case the onset of banding appears closely linked to the presence of a distinctive signature in the shape of the material's time-dependent rheological response function. Importantly, although this signature is specific to the particular flow protocol in question, it appears largely universal for all complex fluids in a given protocol. For example the onset of shear banding in the shear startup protocol appears closely related to the presence of an overshoot in the stress startup signal, as we shall elaborate below.

Motivated by these observations, in a recent letter [Moorcroft and Fielding (2013)] we derived fluid-universal criteria for the onset of linear instability to the formation shear bands, one for each protocol in turn: step stress, shear startup, and step strain. Each criterion depends only on the shape of the experimentally measured rheological response function for that protocol, *independent* of the mesostructure and constitutive dynamics of the particular material in question. These predictions for banding in



**FIG. 1.** Thin line: constitutive curve for an underlying base state of homogeneous shear flow. Homogeneous flow is linearly unstable in the dashed region. Thick lines joined by dotted plateau: corresponding steady state flow curve. For imposed shear rates in the plateau region  $\dot{\gamma}_l < \dot{\gamma} < \dot{\gamma}_h$  the steady state is shear banded (see Fig. 2).

time-dependent flows thus have the same highly general, fluid-universal status as the widely known criterion for banding in steady state (of a negatively sloping constitutive curve).

Whether or not the time-dependent shear bands predicted here persist to steady state of course depends on the shape of that underlying constitutive curve for stationary homogeneous flow. However an important contribution of this work is to highlight that pronounced banding often arises during a fluid's transient evolution to a steady flowing state, given the time-dependent flow signatures that we shall discuss, even in fluids for which the underlying constitutive curve is monotonic and the eventual steady state unbanded (Fig. 2).

The present manuscript provides an in-depth discussion of the criteria outlined in Moorcroft and Fielding (2013), and a thorough numerical exploration of them within two of the most popular models for the rheology of entangled polymeric fluids: the rolle-poly (RP) model and the Giesekus model. Accordingly, it addresses conventional polymeric fluids such as concentrated polymer solutions or melts of high molecular weight; also, entangled wormlike micelles whose long, chain-like substructures undergo the same stress relaxation mechanisms as polymers, with the additional mechanisms of chain breakage and reformation [Cates (1990)]. For convenience we refer to all these materials simply as “polymeric fluids” in what follows. The reader is referred to a separate manuscript for a discussion of the same phenomena in the context of a broad class of disordered soft glassy materials such as foams, dense emulsions, onion surfactants and microgel bead suspensions.

The paper is structured as follows. In Sec. II we survey the experimental and simulation evidence for shear banding in time-dependent flow protocols. In Sec. III we outline a general theoretical framework for the rheology of complex fluids and give details of the rolle-poly and Giesekus constitutive models of polymeric flows. In Sec. IV we detail a linear stability analysis for the onset of shear banding in time-dependent flows, performed within this general framework. In Secs. V–VII we present our analytical criteria for the onset of shear banding in step stress, strain ramp, and shear startup protocols, respectively, and give supporting numerical evidence in each case. We also discuss the way our predictions relate to experimental data. Conclusions and perspectives for further study are given in Sec. VIII.

Throughout the manuscript we use the term “constitutive curve” to describe the relation between shear stress and strain-rate for an underlying base state of homogeneous shear flow. We use the term “flow curve” to describe the relation between shear stress and applied strain-rate  $\bar{\dot{\gamma}}$  (averaged across the sample) for a steady flowing state. In any regime of homogeneous steady state flow, these two curves coincide.

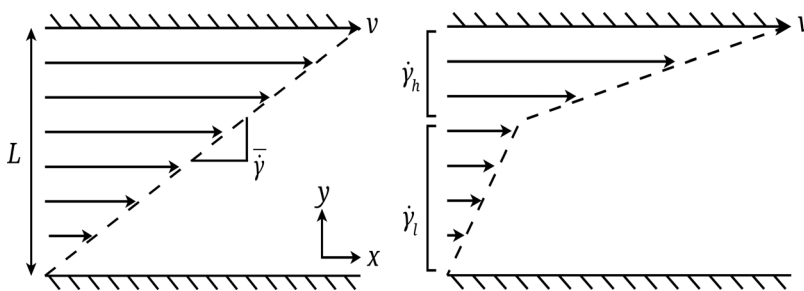


FIG. 2. Left: homogeneous flow profile. Right: shear banded flow profile.

## II. EXPERIMENTAL AND NUMERICAL MOTIVATION

### A. Step stress

Steady state shear banding is associated with a region of negative slope in the underlying constitutive curve of shear stress  $\Sigma$  as a function of shear rate  $\dot{\gamma}$  for an underlying base state of stationary (though not necessarily stable) homogeneous flow. The composite flow curve  $\Sigma(\dot{\gamma})$  for the steady state banded flow then typically displays a flat (or slightly upwardly sloping) plateau spanning a window of shear rates  $\dot{\gamma}_l < \dot{\gamma} < \dot{\gamma}_h$  at (or spanning a small window about) a selected value of the stress  $\Sigma_p$  (see Fig. 1). Accordingly, steady state banding is relatively easily accessed in an applied shear rate protocol for imposed rates  $\dot{\gamma}_l < \dot{\gamma} < \dot{\gamma}_h$ , but much more difficult to access under conditions of a constant imposed stress, which must be tuned to lie in the small window of stress consistent with this near-plateau in the flow curve.

Nonetheless, following the imposition to a previously unloaded sample of a step stress in the vicinity of this plateau  $\Sigma \sim \Sigma_p$ , entangled polymeric materials commonly exhibit time-dependent shear banding [Boukany and Wang (2009a); Hu *et al.* (2007); Tapadia and Wang (2003); Hu *et al.* (2008); Boukany and Wang (2008); Hu and Lips (2005); Hu (2010); Boukany and Wang (2009c)]. Its onset appears closely associated with a sudden and dramatic increase in the shear rate response of the system by several orders of magnitude over a short time interval, as it rises from a small initial value to attain its final value on the steady state flow curve [Ravindranath and Wang (2008); Tapadia and Wang (2003); Hu *et al.* (2008); Boukany and Wang (2008); Hu and Lips (2005); Boukany and Wang (2009c)]. In some cases a return to homogeneous shear is seen as steady state is neared [Boukany and Wang (2009a)], though this is often complicated by the occurrence of edge fracture, which can severely limit the determination of true steady state [Ravindranath and Wang (2008); Inn *et al.* (2005)]. Whether polymeric fluids exhibit steady state banding in the step stress protocol therefore remains an open question.

### B. Strain ramp

In a strain ramp protocol, shear is applied at a constant rate  $\dot{\gamma}_0$  for a time  $t^*$  until some desired strain amplitude  $\gamma_0 = \dot{\gamma}_0 t^*$  is attained, after which the shearing is stopped. The limit  $t^* \rightarrow 0$  and  $\dot{\gamma}_0 \rightarrow \infty$  at fixed  $\gamma_0$  gives a theoretically idealized step strain. Indeed in practice a rapid ramp is often termed a step strain.

The shear stress relaxation function  $\Sigma(t')$  as a function of the time  $t' = t - t^*$  elapsed since the end of the ramp is usually reported after scaling by the strain amplitude to give  $G(t', \gamma_0) = \Sigma(t', \gamma_0)/\gamma_0$ , with  $G(t') = \lim_{\gamma_0 \rightarrow 0} G(t', \gamma_0)$  in the small strain limit of linear response.

This protocol has been extensively studied experimentally in entangled polymeric fluids [Venerus (2005); Osaki and Schrag (1971); Osaki and Kurata (1980); Osaki *et al.* (1982); Larson (1988); Doi and Edwards (1989); Osaki (1993); Einaga *et al.* (1971); Rolón-Garrido and Wagner (2009); Sanchez-Reyes and Archer (2002)]. The stress relaxation function typically shows a double exponential form, with time-strain separability characterised by the so-called “damping function”  $h$  for times greater than some  $t' = \tau_k$

$$h(\gamma_0) = \frac{G(t', \gamma_0)}{G(t')} \quad \text{for } t' \gg \tau_k. \quad (1)$$

Experimental data for this damping function in entangled polymers have been compared extensively with the form predicted theoretically by Doi and Edwards (DE)

[Doi and Edwards (1978); Osaki *et al.* (1982); Rolón-Garrido and Wagner (2009); Sanchez-Reyes and Archer (2002); Osaki and Kurata (1980)]. Review articles [Venerus (2005); Osaki (1993)] suggest that a significant proportion of the available experimental data [Osaki *et al.* (1982); Archer (1999); Islam *et al.* (2001); Vrentas and Graessley (1982)] agrees well with the DE damping function, particularly for moderately entangled melts or solutions. This has been termed type A behaviour. A small number of studies, mostly in very weakly entangled fluids, show a weaker initial stress relaxation in the regime before the time-strain separable domain is reached, leading to a damping function that lies above the Doi-Edwards prediction (type B behaviour). Finally, studies [Osaki and Kurata (1980)] of fluids with high entanglement numbers  $Z \geq 50$  often report a faster stress relaxation before the time-strain separable domain is reached so that the experimental damping function lies below that of Doi and Edwards [Juliani and Archer (2001); Archer (1999); Islam *et al.* (2001); Vrentas and Graessley (1982)] (type C behaviour).

Velocimetric studies in this protocol commonly reveal “macroscopic motions” following a step strain of sufficiently large amplitude  $\gamma_0 \geq 1.5$  in both entangled polymer melts and solutions [Li and Wang (2010); Boukany and Wang (2009b); Wang *et al.* (2006); Ravindranath and Wang (2007); Fang *et al.* (2011); Archer *et al.* (1995)] and wormlike micelles [Boukany and Wang (2008)]. These macroscopic motions refer to non-zero velocities  $v(y, t > t^*) \neq 0$  and associated heterogeneous shear zones, i.e., shear bands, measured locally within the flow cell for some time even once the rheometer plates have stopped moving after the end of the ramp. Wang and co-workers showed that the same fluid can exhibit all three types of behaviour A to C above, depending on the extent of any wall-slip associated with these “macroscopic motions” [Ravindranath and Wang (2007)]: bulk shear in the sample’s interior is usually associated with type A or B behaviour, and wall-slip with type C behaviour.

Theoretically, an instability leading to strain localisation following the imposition of a step strain was proposed in the context of the DE model by Marrucci and Grizzuti (1983). The DE theory predicts a maximum in the shear stress  $\Sigma(t', \gamma_0)$  when it is plotted as a function of applied strain amplitude  $\gamma_0$  for a given time instant  $t' \sim \tau_k$  after the step. This maximum occurs at a strain value of  $\gamma_0 \approx 2$  and results in a negative slope for strain amplitudes beyond this maximum:  $\partial_{\gamma_0} \Sigma(t' \sim \tau_k, \gamma_0) < 0$ . Marrucci and Grizzuti used a free energy calculation to show that step strains with amplitudes in this regime of negative slope are unstable to the onset of heterogeneity.

Numerical studies of the rolie-poly model by Olmsted and co-workers have likewise reported shear rate heterogeneity during stress relaxation after a fast strain ramp of sufficiently large strain amplitude [Adams and Olmsted (2009a, 2009b)] consistent with the predictions of Marrucci and Grizzuti (1983). The form of this heterogeneity is sensitive to the initial noise conditions, and its onset can show a delay after the end of the ramp [Agimelen and Olmsted (2013)]. These results are in qualitative accordance with experiments showing that the onset of macroscopic motions can be delayed after the end of the ramp [Boukany *et al.* (2009); Boukany and Wang (2009b); Archer *et al.* (1995)], with the delay time related to the time taken for polymer chain stretch to relax [Boukany *et al.* (2009); Archer *et al.* (1995)]. Olmsted and co-workers also showed that in extreme cases a very large shear rate can develop across a stationary “fracture” plane so that the local velocity is very difficult to resolve. These results are qualitatively similar to experiments showing a “failure” plane over which the shear rate is extremely high [Fang *et al.* (2011); Boukany *et al.* (2009)]. Shear rate heterogeneity after a fast ramp has also been reported in a two-species elastic network model [Zhou *et al.* (2008)].



### C. Shear startup

In shear startup, a constant shear rate is applied to a previously undeformed sample for all times  $t > 0$ . Time-dependent shear banding has been widely reported in this protocol in entangled polymer solutions and melts [Ravindranath *et al.* (2008); Ravindranath and Wang (2008); Boukany and Wang (2009a); Boukany *et al.* (2009); Boukany and Wang (2009b); Tapadia and Wang (2003); Hu *et al.* (2007); Boukany and Wang (2009c)], and in wormlike micelles [Hu *et al.* (2008); Boukany and Wang (2008)]. Its onset appears closely associated with the presence of an overshoot in the shear stress as it evolves from its initial value of zero to its final value on the ultimate steady state flow curve.

In some materials this time-dependent banding is effectively a precursor to true steady state banding. In such cases it can be viewed as the kinetic process by which these bands develop out of an initially homogeneous startup flow. Nonetheless, the magnitude of the time-dependent banding during startup is often strikingly greater than that which remains in the final steady state [Boukany and Wang (2009a); Ravindranath and Wang (2008); Ravindranath *et al.* (2008); Tapadia and Wang (2006); Boukany and Wang (2009c)]. Indeed, it is often sufficiently dramatic as to be accompanied by elastic-like recoil in which velocities measured locally within the flow cell can even temporarily become negative [Boukany and Wang (2009a); Ravindranath *et al.* (2008); Boukany and Wang (2009c)] such that the fluid is locally and temporarily moving in the direction opposite to that of the rheometer plate that is driving the shear. Furthermore, pronounced but transient banding associated with a stress overshoot is also commonly seen even in less well entangled polymer solutions, for which the final steady flow state is homogeneous [Boukany and Wang (2009a); Hu *et al.* (2007); Ravindranath *et al.* (2008)]. Taken together, this evidence suggests that qualitatively different instability mechanisms might underlie shear banding in startup compared with that in steady state. We return to explore this concept in our discussion of “elastic” versus “viscous” banding instabilities in Sec. VII below.

Numerical studies have likewise reported time-dependent shear banding associated with stress overshoot in startup. Adams and co-workers [Adams and Olmsted (2009a, 2009b); Adams *et al.* (2011)] explored the rolie-poly model of polymeric fluids, which can have either a monotonic or non-monotonic constitutive curve, depending the value of the convective constraint release parameter  $\beta$  and the entanglement number  $Z$ . Their work demonstrated that banding and negative-velocity recoil can arise shortly after a stress overshoot, regardless of whether the underlying constitutive curve is monotonic or non-monotonic. For a non-monotonic constitutive curve this banding persists to steady state, though with a much weaker magnitude than during startup. For a monotonic constitutive curve, homogeneous flow is recovered in steady state. Adams *et al.* (2011) also discussed carefully the effects of rheometer cell curvature on these phenomena. Banding in startup has also been reported in simulations of a two-species elastic network model [Zhou *et al.* (2008)]; and in molecular dynamics simulations of polymer melts [Cao and Likhtman (2012)].

## III. MODELS

### A. Force balance

The stress response of a complex fluid to an applied deformation is dominated by the behaviour of its internal mesoscopic substructures [Larson (1999)]. For example, a polymeric fluid comprises many chain-like molecules, the entanglements between which



result in topological constraints on their molecular motion. We therefore decompose the total stress  $\Sigma$  into a viscoelastic contribution from these mesoscopic substructures, as well as a familiar Newtonian contribution of viscosity  $\eta$ , and an isotropic pressure

$$\Sigma = G(\mathbf{W} - \mathbf{I}) + 2\eta\mathbf{D} - p\mathbf{I}. \quad (2)$$

The viscoelastic contribution  $\sigma = G(\mathbf{W} - \mathbf{I})$  is expressed in terms of a constant elastic modulus  $G$  and a tensor  $\mathbf{W}(\mathbf{r}, t)$ , which describes the local conformation of the mesoscopic substructures. The dynamics of this conformation tensor in flow is prescribed by a viscoelastic constitutive equation. In Sec. III B, we introduce the constitutive equations that we shall use throughout this work. The Newtonian contribution  $2\eta\mathbf{D}$  may arise from the presence of a true solvent, or may represent viscous stresses arising from any fast degrees of freedom of the polymer chains that are not ascribed to the viscoelastic contribution. Here  $\mathbf{D} = \frac{1}{2}(\mathbf{K} + \mathbf{K}^T)$  where  $K_{\alpha\beta} = \partial_\beta v_\alpha$  and  $\mathbf{v}(\mathbf{r}, t)$  is the fluid velocity field. The isotropic pressure field  $p(\mathbf{r}, t)$  is determined by the condition of incompressible flow

$$\nabla \cdot \mathbf{v} = 0. \quad (3)$$

Throughout we consider the limit of zero Reynolds number, in which the force balance condition states that the stress tensor  $\Sigma$  must remain divergence free

$$\nabla \cdot \Sigma = 0. \quad (4)$$

In taking this limit we are assuming that the timescale for inertially driven diffusion of momentum across the sample is small compared to the fluid's viscoelastic relaxation timescale. In practice, any residual spatial heterogeneity associated with the finite timescale of momentum diffusion could provide an additional source of seeding for the initial onset of shear bands, as noted in Sec. IV B below. The interplay of inertia with shear banding was recently explored by [Zhou \*et al.\* \(2012\)](#).

## B. Viscoelastic constitutive equation

The rheological response of an entangled polymeric fluid can be modelled from a microscopic starting point by considering a test polymer chain that has its dynamics laterally constrained by topological entanglements with other chains. These entanglements are then represented in mean field spirit by an effective “tube” [[Doi and Edwards \(1989\)](#)]. The GLAMM model [[Graham \*et al.\* \(2003\)](#)] provides a fully microscopic stochastic equation of motion for such a test chain and its tube. However it is computationally intensive to work with in practice. An approximation was therefore derived by [Likhtman and Graham \(2003\)](#) who projected the full GLAMM model onto a single-mode description, known as the RP model. This gives the viscoelastic constitutive equation for the dynamics of the conformation tensor as

$$\partial_t \mathbf{W} + \mathbf{v} \cdot \nabla \mathbf{W} = \mathbf{K} \cdot \mathbf{W} + \mathbf{W} \cdot \mathbf{K}^T - \frac{1}{\tau_d}(\mathbf{W} - \mathbf{I}), \quad (5)$$

$$- \frac{2(1-A)}{\tau_R} [\mathbf{W} + \beta A^{-2\delta}(\mathbf{W} - \mathbf{I})] + D \nabla^2 \mathbf{W}. \quad (6)$$

Here  $A = \sqrt{3/T}$ , where  $T = \text{tr } \mathbf{W}$  denotes the magnitude of chain stretch. The reptation time  $\tau_d$  is the timescale on which a test chain escapes its tube of constraints by

undergoing 1D curvilinear diffusion along its own length. The Rouse time  $\tau_R$  is the much shorter timescale on which chain stretch relaxes. The ratio of these two relaxation times is prescribed by the number of entanglements per chain  $Z$  [Doi and Edwards (1989)], with  $\tau_d/\tau_R = 3Z$ . Throughout Secs. V–VII, we quote values for  $\tau_R$ , with the understanding that the corresponding value for  $Z$  is then immediately prescribed in each case as  $Z = 1/3\tau_R$  in our units for which  $\tau_d = 1$ . The parameter  $\beta$  describes the efficacy of so-called convective constraint release (CCR) events, in which relaxation of polymer chain stretch also relaxes entanglement points, thereby also allowing relaxation of tube orientation. It has range  $0 \leq \beta \leq 1$ . The parameter  $\delta$  also describes CCR. Following Likhtman and Graham (2003) we set  $\delta = -\frac{1}{2}$  throughout. Depending on the values of the model parameters, the constitutive curve of the RP model can either be monotonic or non-monotonic.

The value of  $\beta$  is difficult to relate directly to experiment and there is no consensus on its correct value, though a small value was used by Likhtman and Graham (2003) to best fit experimental data in flow protocols that were assumed to be homogeneous. A more recent study [Agimelen and Olmsted (2013)] aimed at describing “fracture-like” velocity profiles after a step strain likewise found a good fit to experimental findings only for small values of  $\beta$ .

For  $\beta = 0$  the rolie-poly model in its non-stretching limit  $\tau_R \rightarrow 0$  maps on to the microscopically derived reptation–reaction model for the nonlinear rheology of reversibly breakable wormlike micelles [Cates (1990)], once a decoupling approximation is employed to express fourth order moments of the tube segment orientation distribution as products of second order moments.

The diffusive term  $D\nabla^2\mathbf{W}$  was absent in the original formulation of the model. Without it, however, the interface between the shear bands is unphysically sharp, with a discontinuity in the shear rate profile  $\dot{\gamma}(y)$  across it. Furthermore the total shear stress of a steady shear banded state is not uniquely selected, but depends on the shear history to which the material has been subject [Olmsted *et al.* (2000)]. This contradicts experimental findings, which find a unique plateau stress  $\Sigma_p$ . The diffusive term lifts this degeneracy to give a uniquely selected stress as well as a characteristic width to the interface between the bands that scales as  $\sqrt{D\tau_d}$  [Lu *et al.* (2000); Olmsted *et al.* (2000)], though with a prefactor that can become large near a critical point [Fielding and Olmsted (2003b)].

A more phenomenologically motivated constitutive equation for concentrated polymeric solutions or melts considers an anisotropic drag on polymer chains that are oriented due to flow. Representing these chains simply as dumbbells, Giesekus (1982) began with the upper convected Maxwell model for dilute solutions and incorporated into it an anisotropy parameter  $\alpha$  with  $0 \leq \alpha \leq 1$ . The resulting constitutive equation has the form

$$\partial_t \mathbf{W} + \mathbf{v} \cdot \nabla \mathbf{W} = \mathbf{K} \cdot \mathbf{W} + \mathbf{W} \cdot \mathbf{K}^T - \frac{1}{\lambda}(\mathbf{W} - \mathbf{I}) - \frac{\alpha}{\lambda}(\mathbf{W} - \mathbf{I})^2 + D\nabla^2 \mathbf{W}, \quad (7)$$

where  $\lambda$  is the relaxation time. A diffusive term is again included to properly describe a shear banding flow.

This Giesekus model admits either non-monotonic or monotonic constitutive curves, depending on the value of  $\alpha$  and the solvent viscosity  $\eta$ . It has been successful in modelling the steady state shear banding properties of entangled wormlike micelles [Helgeson *et al.* (2009a, 2009b)], and a multi-mode equivalent has shown good agreement with the experimentally measured steady shear viscosity [Byars *et al.* (1997); Quinzani *et al.* (1990); Burdette (1989); Azaiez *et al.* (1996)] and damping function [Khan and Larson (1987)] of polymeric materials.

### C. Flow geometry and boundary conditions

Throughout we consider a sample of fluid sandwiched between parallel plates at  $y = \{0, L\}$ , sheared by moving the top plate in the  $\hat{x}$  direction. Translational invariance is assumed in the  $\hat{x}, \hat{z}$  directions. The fluid velocity is then of the form  $\mathbf{v} = v(y, t)\hat{x}$ , and the local shear rate

$$\dot{\gamma}(y, t) = \partial_y v(y, t). \quad (8)$$

The spatially averaged (or “global”) shear rate is

$$\bar{\dot{\gamma}}(t) = \frac{1}{L} \int_0^L \dot{\gamma}(y, t) dy. \quad (9)$$

Note that in assuming planar Couette flow and in allowing spatial heterogeneity only in the main banding direction  $y$ , we have eliminated upfront the possibility of a viscoelastic Taylor Couette instability [Larson *et al.* (1990)], which might interact with [Fielding (2010)] the basic banding phenomenon of interest here at very high applied shear rates. The assumption of planar Couette flow also eliminates any gradients in the total (polymeric plus solvent) shear stress, which, as discussed in Sec. IV B below, might act as one possible source of seeding the banding instability of interest here [Adams *et al.* (2011)].

We assume boundary conditions at the plates of no-slip for the velocity

$$v = 0 \quad \text{at} \quad y = 0 \quad \text{and} \quad v = \bar{\dot{\gamma}}L \quad \text{at} \quad y = L, \quad (10)$$

and zero gradient for every component of the polymeric conformation tensor

$$\partial_y W_{ij} = 0 \quad \text{at} \quad y = 0, L \quad \forall \quad i, j. \quad (11)$$

The condition of no permeation for the velocity is automatically guaranteed by our assumption of unidirectional flow.

### D. Componentwise equations

In the flow geometry just described, the condition of incompressible flow [Eq. (3)] is automatically satisfied. The force balance condition of creeping flow [Eq. (4)] demands that the total shear stress is uniform across the cell  $\partial_y \Sigma_{xy} = 0$ . The viscoelastic and Newtonian solvent contributions may however each vary in space, provided their sum remains uniform

$$\Sigma_{xy}(t) = G W_{xy}(y, t) + \eta \dot{\gamma}(y, t). \quad (12)$$

Componentwise the RP model reduces to a system of three dynamical variables

$$\begin{aligned} \dot{W}_{xy} &= \dot{\gamma} W_{yy} - \frac{W_{xy}}{\tau_d} - \frac{2(1-A)}{\tau_R} (1 + \beta A) W_{xy} + D \partial_y^2 W_{xy}, \\ \dot{W}_{yy} &= -\frac{W_{yy} - 1}{\tau_d} - \frac{2(1-A)}{\tau_R} [W_{yy} + \beta A (W_{yy} - 1)] + D \partial_y^2 W_{yy}, \\ \dot{T} &= 2\dot{\gamma} W_{xy} - \frac{T - 3}{\tau_d} - \frac{2(1-A)}{\tau_R} [T + \beta A (T - 3)] + D \partial_y^2 T. \end{aligned} \quad (13)$$

In the limit of fast chain stretch relaxation  $\tau_R \rightarrow 0$  this reduces to a simpler system of two dynamical variables

$$\begin{aligned}\dot{W}_{xy} &= \dot{\gamma} \left[ W_{yy} - \frac{2}{3}(1 + \beta)W_{xy}^2 \right] - \frac{1}{\tau_d} W_{xy}, \quad + D \partial_y^2 W_{xy}, \\ \dot{W}_{yy} &= \frac{2}{3} \dot{\gamma} [\beta W_{xy} - (1 + \beta)W_{xy}W_{yy}] - \frac{1}{\tau_d} (W_{yy} - 1) + D \partial_y^2 W_{yy},\end{aligned}\tag{14}$$

with a constant molecular trace  $T = 3$ . We shall refer to this “non-stretching” form below as the non-stretch rolie-poly (nRP) model; and the full “stretching” version of Eq. (13) as the sRP model.

The Giesekus model likewise reduces to a system of three dynamical variables

$$\begin{aligned}\dot{W}_{xy} &= \dot{\gamma} W_{yy} - \frac{W_{xy}}{\lambda} - \frac{\alpha W_{xy}}{\lambda} [(W_{xx} - 1) + (W_{yy} - 1)] + D \partial_y^2 W_{xy}, \\ \dot{W}_{xx} &= 2W_{xy} \dot{\gamma} - \frac{W_{xx} - 1}{\lambda} - \frac{\alpha}{\lambda} [W_{xy}^2 + (W_{xx} - 1)^2] + D \partial_y^2 W_{xx}, \\ \dot{W}_{yy} &= -\frac{W_{yy} - 1}{\lambda} - \frac{\alpha}{\lambda} [W_{xy}^2 + (W_{yy} - 1)^2] + D \partial_y^2 W_{yy}.\end{aligned}\tag{15}$$

We note an important distinction in the structure of these equations. In particular, in the stretching rolie-poly model Eq. (13) and the Giesekus model Eq. (15), the terms prefactored by  $\dot{\gamma}$  are of simple linear form, whereas the terms prefactored by the inverse relaxation timescales are nonlinear. Conversely in the nonstretch rolie-poly model the terms prefactored by  $\dot{\gamma}$  are nonlinear, whereas the terms prefactored by the inverse relaxation timescales are linear. Because the terms prefactored by  $\dot{\gamma}$  dominate the response of a material to a fast shear startup and fast strain ramp, this distinction will be important in what follows, particularly with regards the onset of what we shall term “elastic instability.”

## E. General framework

Motivated by the preceding discussion, we now outline a general theoretical framework for the planar shear flow of complex fluids. This will encompass as special cases the rolie-poly and Giesekus models just described, as well as many other models for the rheology of complex fluids. It is within this general framework that we shall below perform a linear stability analysis to derive fluid-universal criteria for the onset of shear banding in time-dependent flows [Moorcroft and Fielding (2013)]. Accordingly, the results that we obtain should apply to all complex fluids that can be described by a rheological constitutive equation of the highly general form that we propose here.

We begin by combining all dynamical variables relevant to the fluid in question into a state vector  $\mathbf{s}$ . In a polymeric fluid this will include all components of the viscoelastic conformation tensor  $\mathbf{W}$  discussed above,  $\mathbf{s} = (W_{xy}, W_{xx}, W_{yy}, \dots)^T$ . In soft glassy materials it would also include fluidity variables capable of describing the slow evolution of a material into a progressively more solid-like state.

Next we define a projection vector  $\mathbf{p} = (1, 0, 0, \dots)$  to select out of this state vector the shear component  $W_{xy}$  of the viscoelastic conformation variable. The total shear stress  $\Sigma_{xy} = \Sigma$  is then written

$$\Sigma(t) = G\mathbf{p} \cdot \mathbf{s}(y, t) + \eta \dot{\gamma}(y, t).\tag{16}$$

Here and below we drop the  $xy$  subscript from the shear component  $\Sigma$  of the total stress for clarity.

In a planar shear flow, the viscoelastic constitutive equation has the generalised form

$$\partial_t \mathbf{s} = \mathbf{Q}(\mathbf{s}, \dot{\gamma}) + D \partial_y^2 \mathbf{s}. \quad (17)$$

The choice of constitutive model then specifies the functional form of  $\mathbf{Q}$ . Depending on this choice we can obtain, for example, the rolie-poly [Likhtman and Graham (2003)], Giesekus [Giesekus (1982)], Johnson-Segalman [Johnson and Segalman (1977)] or (for an infinite dimensional  $\mathbf{s}$ ) soft glassy rheology model [Hebraud *et al.* (1997)], and many more besides. The compact notation introduced in this subsection therefore includes the behaviour in shear of any fluid described in Subsections III A–III D. Crucially, however, we shall not need to specify  $\mathbf{Q}$  in order to perform our linear stability analysis for the onset of banding. Our stability results will therefore be generic to all models described by a constitutive equation of this highly general form.

## F. Units and parameters

Throughout we choose units in which the rheometer gap width  $L = 1$ ; the elastic modulus  $G = 1$ ; and the terminal viscoelastic relaxation time  $\tau_d = 1$  (RP model) or  $\lambda = 1$  (Giesekus model).

Our choice of time units means that shear rates reported below are actually Weissenberg numbers ( $Wi = \dot{\gamma}\tau$ ) and that times are inverse Deborah numbers ( $De = t/\tau$ ). In this way, the transient “elastic instabilities” that we shall discuss in Sec. VII arise for evolving values of  $1/De$  at fixed  $Wi$ , whereas steady state “viscous instabilities” arise in the regime of non-linear viscoelastic effects (large  $Wi$ ) in the limit  $De \rightarrow \infty$ .

In our nonlinear simulations we shall set the value of the diffusion constant  $D$  such that the interface between the bands has a typical thickness  $\ell = 10^{-2}L$ , thereby placing ourselves in a regime far enough from any critical point [Fielding and Olmsted (2003b)] that the fluid’s intrinsic lengthscales are small compared with the system size and finite size effects are unimportant. In our linear stability analysis we neglect the diffusive terms since they do not affect the results for the long wavelength (system size) modes of interest here, which dominate the initial onset of banding.

This leaves as parameters to be explored the solvent viscosity  $\eta$ , the CCR parameter  $\beta$  (nRP and sRP models), the stretch relaxation time  $\tau_R$ , which specifies  $Z = 3/\tau_R$  in our units (sRP model), and the anisotropy parameter  $\alpha$  (Giesekus model).

## IV. LINEAR STABILITY ANALYSIS

In this section we outline a linear stability analysis to determine whether a state of initially homogeneous shear flow, which we shall call the underlying “base state,” becomes unstable to the growth of heterogeneous perturbations that are the precursor of a shear banded state. Distinct from more conventional linear stability analyses, we are concerned here with a base state that is time-dependent, comprising the initially homogeneous dynamical response of the fluid following the imposition of a step stress, step strain, or shear startup. Accordingly, our analysis follows previous time-dependent ones by Adams *et al.* (2011), Fielding and Olmsted (2003a), and Manning *et al.* (2007).

### A. Equations of motion for heterogeneous perturbations

Working within the general framework set out in Sec. III E, we start by expressing the response of the system to the imposed flow protocol (step stress, strain ramp, shear

startup) as the sum of a time-dependent homogeneous base state plus any (initially) small heterogeneous perturbations

$$\begin{aligned}\Sigma(t) &= \Sigma_0(t), \\ \dot{\gamma}(y, t) &= \dot{\gamma}_0(t) + \sum_{n=1}^{\infty} \delta \dot{\gamma}_n(t) \cos(n\pi y/L), \\ s(y, t) &= s_0(t) + \sum_{n=1}^{\infty} \delta s_n(t) \cos(n\pi y/L).\end{aligned}\tag{18}$$

We have added cosine perturbation terms only to be consistent with the boundary conditions in Eqs. (10) and (11) above. The first of these equations lacks the heterogeneous perturbations seen in the other two because the total shear stress must remain uniform across the sample, according to the force balance condition. The time-dependence of the base state is clearly such that in a step stress protocol  $\Sigma_0(t) = \Sigma_0 = \text{const.}$ ; during a strain ramp  $\dot{\gamma}_0(t) = \dot{\gamma}_0 = \text{const.}$  with  $\dot{\gamma}_0 = 0$  post-ramp; and during a shear startup  $\dot{\gamma}_0(t) = \dot{\gamma}_0 = \text{const.}$

Substituting Eq. (18) into Eqs. (16) and (17), neglecting the diffusive terms as noted above, and expanding in successive powers of the magnitude of the small perturbations  $\delta \dot{\gamma}_n, \delta s_n$ , we find at zeroth order that the homogeneous base state obeys

$$\begin{aligned}\Sigma_0(t) &= G\mathbf{p} \cdot s_0(t) + \eta \dot{\gamma}_0(t), \\ \dot{s}_0 &= \mathbf{Q}(s_0, \dot{\gamma}_0).\end{aligned}\tag{19}$$

At first order, the heterogeneous perturbations obey

$$\begin{aligned}0 &= G\mathbf{p} \cdot \delta s_n(t) + \eta \delta \dot{\gamma}_n(t), \\ \delta \dot{s}_n &= \mathbf{M}(t) \cdot \delta s_n + \mathbf{q} \delta \dot{\gamma}_n,\end{aligned}\tag{20}$$

in which  $\mathbf{M} = \partial_s \mathbf{Q}|_{s_0, \dot{\gamma}_0}$  and  $\mathbf{q} = \partial_{\dot{\gamma}} \mathbf{Q}|_{s_0, \dot{\gamma}_0}$ . These two linearised equations can be combined to give

$$\delta \dot{s}_n = \mathbf{P}(t) \cdot \delta s_n,\tag{21}$$

in which

$$\mathbf{P}(t) = \mathbf{M}(t) - \frac{G}{\eta} \mathbf{q}(t) \mathbf{p}.\tag{22}$$

We neglect terms of second order and above.

In what follows our first objective will be to determine whether at any time  $t$  the heterogeneous perturbations  $\delta \dot{\gamma}_n, \delta s_n(t)$  have a negative or positive rate of growth, respectively indicating linear stability or instability to the onset of shear banding. Our second objective is to relate the onset of growth in these heterogeneous perturbations, i.e., the onset of shear banding, to any distinctive signature in the shape of the experimentally measured rheological response function as specified by the evolution of the underlying homogeneous base state in any given protocol.

We shall tackle these objectives using three different methods that we cross-check against each other. First, we denote by  $\omega(t)$  the real part the eigenvalue of  $\mathbf{P}(t)$  that has the largest real part at any time  $t$ . A positive  $\omega(t)$  strongly suggests that heterogeneous

perturbations will be instantaneously growing at that time  $t$ . This concept of a time-dependent eigenvalue must, however, be treated with caution [Schmid (2007)]. Therefore second, and better, we directly integrate the linearised Eq. (21) using an Euler time-stepping method, carefully converged with respect to reducing the timestep. We examine the time-evolution of the heterogeneous perturbations thereby calculated, to see whether at any instant they are growing or decaying. Finally, we integrate the full non-linear spatio-temporal Eqs. (16) and (17) using a Crank Nicolson algorithm [Press *et al.* (1992)], carefully checked for convergence with respect to the size of the time- and space-steps. The heterogeneous part of the solution of this third method must coincide with the results of the second method as long as the system remains in the linear regime of small perturbations.

As written above, the stability matrix  $\mathbf{P}$  appears to show no dependence on the spatial lengthscale of the perturbation, as denoted by  $n$ . The same comment therefore applies to the eigenvalues of  $\mathbf{P}$ . This follows from our having neglected the diffusive term in the viscoelastic constitutive equation before performing the linearisation. Reinstating the diffusive term would simply transform any eigenvalue  $\omega \rightarrow \omega_n = \omega - Dn^2\pi^2/L^2$  and act to damp out any perturbations with a wavelength of order the microscopic lengthscale  $l$  or below. Accordingly the results of our stability analysis apply only to perturbations of macroscopic lengthscale, which are the ones of interest in the initial formation of shear bands.

## B. Seeding the heterogeneous perturbations

So far, we have discussed how to determine whether heterogeneous perturbations to the homogeneous base state grow or decay over time. We now consider how such perturbations are seeded into the system in the first place. We identify several different possible physical mechanisms for this, including (a) residual heterogeneities that remain in the fluid following initial sample preparation, (b) residual heterogeneities associated with the finite timescale for the diffusion of momentum across the sample in a shear startup, (c) true thermal noise, or (d) stress gradients arising from slight rheometer device curvature in a curved Couette or cone-and-plate geometry, which adds a small systematic perturbation [Adams *et al.* (2011)] to the componentwise equations that we wrote above within the assumption of a theoretically idealised planar geometry.

Of these, we model (a) by adding a small heterogeneous perturbation once only, before the onset of deformation, by initialising  $\delta s_n(t=0) = q\mathbf{X}\delta_{n1}$  for the Fourier modes of the linearised equations, or correspondingly  $\delta s(y, t=0) = qX\cos(n\pi y/L)$  with  $n=1$  in the full spatio-temporal equations ( $\delta_{nm}$  is the Kronecker delta function, equal to 1 if  $n=m$  and equal to 0 otherwise.). This initial perturbation has magnitude  $q$ , which we treat as a parameter of our study.  $\mathbf{X}$  is a vector of the same dimension as the vector  $\mathbf{s}$ . Each of its components is a random number drawn from a uniform distribution of mean 0 and width 1. We choose to seed only the lowest mode  $n=1$  because it is always the most unstable (or least stable) one: as discussed above, the diffusive terms render modes of higher  $n$  less unstable (or more stable).

The results presented below follow the method of seeding (a) just described unless otherwise stated. In some cases we also check these results against scenarios (b) and (c), modelled by adding a small heterogeneous perturbation  $q\sqrt{dt}\mathbf{X}\delta_{n1}$  at every timestep (of duration  $dt$ ) to the Fourier modes of the linearised equations, or correspondingly  $q\sqrt{dt}X\cos(\pi y/L)$  at every timestep in the full spatio-temporal simulation. A new random vector  $\mathbf{X}$  is selected at each timestep. In this case we first evolve the system under conditions of no applied flow or loading but subject to this continuous noise, until a statistically



steady state is reached that correctly captures the fluctuation spectrum of the system in zero shear. We then evolve the chosen flow protocol, also subject to this continuous noise.

For the linearised equations subject to continuous noise, it is furthermore possible to perform an upfront analytical average (denoted  $\langle \rangle$ ) over infinitely many noise histories by evolving the variance of the perturbations

$$\partial_t \mathbf{S} = \mathbf{P} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{P}^T + \mathbf{N}, \quad (23)$$

in which  $\mathbf{S}(t) = \langle \delta \mathbf{s}_n(t) \cdot \delta \mathbf{s}_n^T(t) \rangle$  and  $\mathbf{N}(t)$  is a diagonal matrix characterising the amplitude of the added noise. Using the linearised force balance condition we then easily obtain the evolution of the variance of the shear rate perturbations  $\langle \delta \dot{\gamma}_n^2 \rangle(t)$ .

Besides assuming the noise to be small compared with the background state, we have not attempted to estimate the size of the noise in a quantitative way because it would depend on which source (a)–(d) dominated in practice. We note however that in principle the amplitude in case (d) could be estimated from the size of the device curvature (often about 10%), in (c) using the fluctuation–dissipation theorem and in (b) by considering the finite timescale of momentum diffusion (set by  $\rho L^2/\eta$  where  $\rho$  is the density and  $L$  the gap size) compared to the viscoelastic relaxation time. The amplitude in case (a) would depend on the loading protocol, and so be harder to estimate. We also remark that in any numerical evolution of the linearised equations the overall amplitude is technically irrelevant, because the assumption of infinitesimal amplitude has already been made in making the linearisation.

### C. Reporting the heterogeneous perturbations

For the linearised system subject to seeding (a) above we report the size of the shear rate heterogeneity as  $|\delta \dot{\gamma}_{n=1}|(t)$ . For a linearised system subject to continuous noise (b), (c) we report  $\sqrt{\langle \delta \dot{\gamma}_{n=1}^2 \rangle}(t)$ . In the full nonlinear spatiotemporal simulation we quantify the degree of heterogeneity by the difference at any time between the maximum and minimum values of the shear rate across the cell

$$\Delta \dot{\gamma}(t) = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}. \quad (24)$$

We often below refer to this quantity as the “degree of banding.”

We have checked that as long as the nonlinear simulation remains in the linear regime of small heterogeneity, the  $\Delta \dot{\gamma}$  that it predicts evolves in the same way as the perturbations calculated in the corresponding linearised calculation, up to a constant prefactor  $O(1)$ .

## V. RESULTS: STEP STRESS

In this section we present our results for time-dependent shear banding during a system’s creep response following the imposition of a step shear stress to a previously unloaded sample,  $\Sigma(t) = \Sigma_0 \Theta(t)$ . We start in Sec. [VA](#) by developing an analytical criterion for the onset of banding. In Secs. [VB](#) and [VC](#) we give numerical results to support this prediction, in the rolie-poly and Giesekus models, respectively.

### A. Criterion for shear banding following a step stress

Here we develop a criterion for the onset of shear banding in the step stress protocol. We do so by considering an underlying base state of initially homogeneous flow response

to the applied loading, and the dynamics of small heterogeneous perturbations about this base state.

Following the imposition of a step shear stress to a previously unloaded sample, it is easy to show by time-differentiating Eq. (19) subject to the constraint  $\Sigma_0(t) = \Sigma_0$  that any underlying base state of initially homogeneous flow response must obey

$$\frac{d}{dt}\dot{s}_0 = (\mathbf{M} - G\mathbf{q}\mathbf{p}/\eta) \cdot \dot{s}_0. \quad (25)$$

Equations (21) and (22) together show that any heterogeneous perturbations to this base state must obey

$$\frac{d}{dt}\delta s_n = (\mathbf{M} - G\mathbf{q}\mathbf{p}/\eta) \cdot \delta s_n. \quad (26)$$

Comparing these two equations, we see that the heterogeneous perturbations  $\delta s_n$  obey the same dynamical equation as the time-derivative of the homogeneous base state  $\dot{s}_0$ . Combined with the force balance condition [Eq. (4)] and its linearised counterpart, this means that heterogeneous shear rate perturbations must grow, and shear bands develop

$$\frac{d\delta\dot{\gamma}_n}{dt} / \delta\dot{\gamma}_n > 0, \quad (27)$$

in any regime where

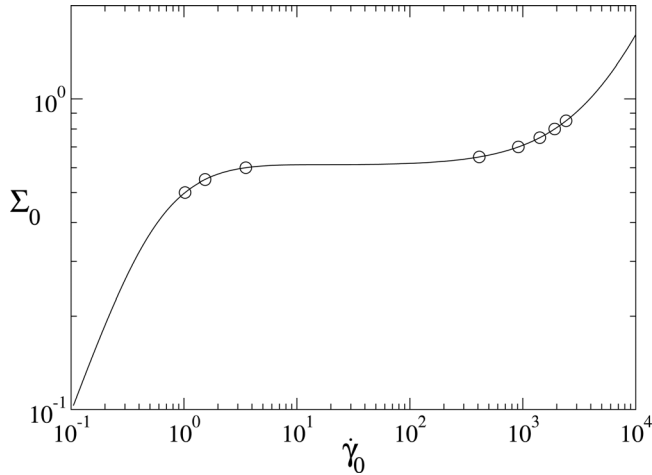
$$\frac{d^2\dot{\gamma}_0}{dt^2} / \frac{d\dot{\gamma}_0}{dt} > 0. \quad (28)$$

This important result tells us that a state of initially homogeneous creep response to an imposed step stress becomes linearly unstable to the onset of shear banding whenever its shear rate signal  $\dot{\gamma}_0(t)$  is simultaneously upwardly curving and upwardly sloping in time (Alternatively  $\dot{\gamma}_0(t)$  may be simultaneously downwardly curving and downwardly sloping, though in practice we have never seen this numerically.).

How does this time-differentiated creep curve  $\dot{\gamma}_0(t)$  of the underlying homogeneous base state relate to the time-differentiated creep curve  $\dot{\gamma}(t)$  measured experimentally by recording the motion of the rheometer plates? Clearly, in any regime before banding sets in these two quantities coincide by definition. Once shear banding fluctuations have grown appreciably into the nonlinear regime, however, the two need not coincide. Nevertheless, in our numerical studies of step stress in the rolie-poly and Giesekus models (and also of the soft glassy rheology model that we will report in a future publication we have never observed the globally measured bulk shear rate signal to be strongly affected, in overall shape at least, by the presence of shear banding within the fluid. Accordingly we can take Eq. (28) to apply also to the experimentally measured signal  $\bar{\gamma}(t)$ . Experimentalists should therefore be alert to the onset of shear banding in any creep experiment where the time-differential of the measured creep curve simultaneously shows upward slope and upward curvature: bulk rheological data can be used as a predictor of the presence of shear banding, even in the absence of accompanying velocimetric data.

## B. Numerical results: Rolie-poly model

Having developed an analytical criterion for the onset of shear banding following the imposition of a step stress, we now present numerical results that support it. Figure 3

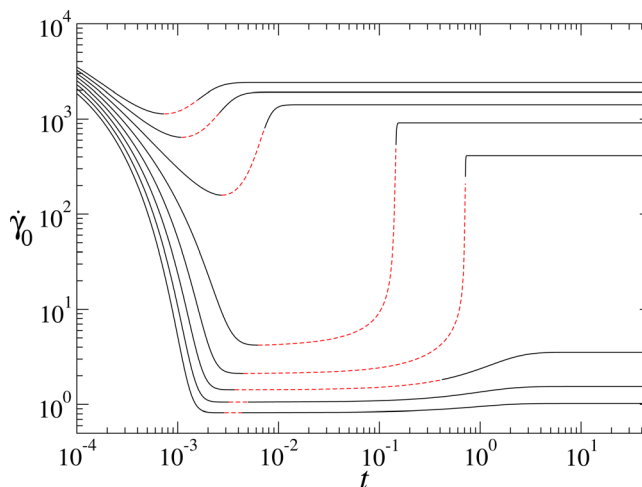


**FIG. 3.** Steady state constitutive curve in the rolie-poly model. Symbols correspond to steady states from Fig. 4. Parameters:  $\beta = 0.8$ ,  $\eta = 10^{-4}$ ,  $\tau_R = 0.0$ .

shows the underlying constitutive curve of stress as a function of strain-rate in the rolie-poly model for a value of the CCR parameter  $\beta = 0.8$ . Because this curve is monotonic, the eventual steadily flowing state is homogeneous.

Nonetheless for imposed stress values in the relatively flat region of this curve, we might expect shear bands to form transiently as the system evolves towards its steady state on this ultimate constitutive curve. Motivated by this expectation, we now study numerically the step stress protocol for the stress values denoted by circles in Fig. 3.

We report first results for the underlying time-dependent base state of homogeneous creep response to this imposed load, obtained in a numerical calculation in which the flow is artificially constrained to remain homogeneous. The shear rate evolution  $\dot{\gamma}_0(t)$  in this case is shown in Fig. 4. Immediately after loading the solvent bears all the applied stress and  $\dot{\gamma}_0(t = 0^+) = \Sigma_0/\eta$ . The shear rate then shows a rapid early decay on a

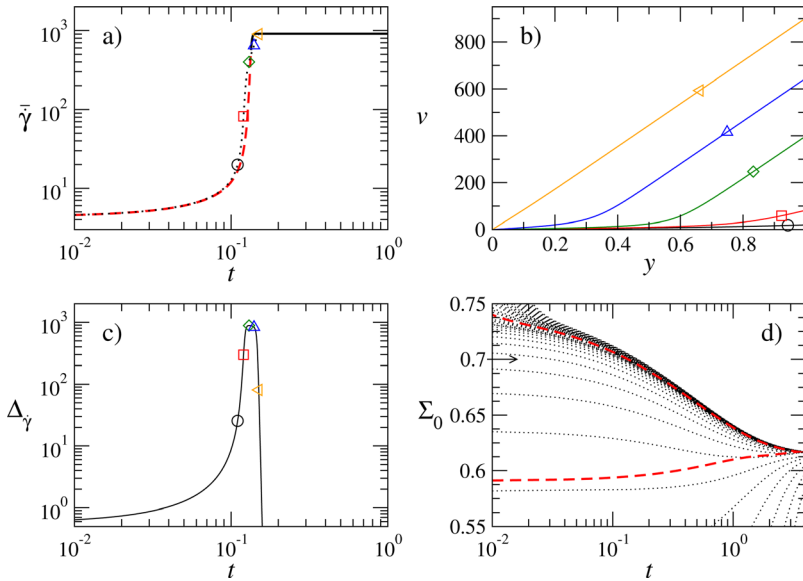


**FIG. 4.** Shear rate as a function of time for imposed shear stresses  $\Sigma_0 = 0.5, 0.55, \dots, 0.85$  (curves bottom to top at fixed  $t$ ) in the (homogeneously constrained) RP model. Dashed lines show regions of linear instability,  $\partial_t^2 \dot{\gamma}_0 / \partial_t \dot{\gamma}_0 > 0$ . Steady states correspond to the circles in Fig. 3. Parameters:  $\beta = 0.8$ ,  $\eta = 10^{-4}$ ,  $\tau_R = 0.0$ .

timescale that appears numerically to scale as  $O(\sqrt{\eta \tau_d / G})$ , but that may not be accessible experimentally due to inertial effects such as creep ringing that we have neglected here (Our numerics set any inertial timescales to zero.). Following this fast initial drop, the shear rate subsequently displays a regime of simultaneous upwards curvature and upwards slope, shown by dashed lines in the figure. In this regime, this underlying base state of homogeneous flow is predicted by our criterion (28) above to become linearly unstable to the onset of shear rate heterogeneity.

Accordingly, in Figs. 5(a)–5(c) we show the results of a fully nonlinear simulation that now permits heterogeneity in the flow-gradient direction. Inset (a) shows the evolution of the global shear rate  $\dot{\gamma}(t)$  for a single stress value  $\Sigma = 0.7$ , near the point of weakest slope of the constitutive curve in Fig. 4. As can be seen, this bulk rheological signal differs little from that given by our earlier homogeneous calculation:  $\dot{\gamma}(t) \approx \dot{\gamma}_0(t)$ , even in the regime where bands form and the two signals might be expected to differ. This supports our claim made above that the theoretical criterion of Eq. (28), which strictly applies only to the underlying base state  $\dot{\gamma}_0(t)$ , can also be applied to the experimentally measured bulk signal  $\dot{\gamma}(t)$ .

Inset (b) shows snapshots of the velocity profiles that accompany the bulk signal of (a). These clearly exhibit macroscopic shear banding. Plotting the associated degree of banding  $\Delta\dot{\gamma}(t) = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}$  as a function of time in (c), we find good agreement with our prediction (28). Banding sets in once  $\dot{\gamma}$  shows upward curvature. The flow then returns to be homogeneous once  $\dot{\gamma}$  exhibits downward curvature during the final stage of its evolution to steady state.

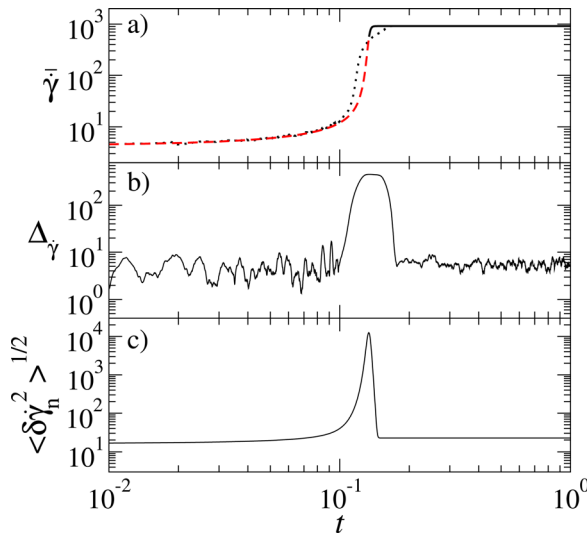


**FIG. 5.** Step stress of amplitude  $\Sigma_0 = 0.7$  in the RP model. (a) Thick line: global shear rate in a homogeneously constrained system, with the dashed region denoting  $\partial_t^2 \dot{\gamma}_0 / \partial_t \dot{\gamma}_0 > 0$ . Dotted line shows corresponding signal with heterogeneity allowed,  $\dot{\gamma}$ . (b) Snapshots of the velocity profile at times corresponding to symbols in (a). (c) Corresponding degree of banding  $\Delta\dot{\gamma} = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}$ . (d) Banding dynamics in the full plane of stress versus time. A horizontal slice across this plane corresponds to a single run at a constant imposed stress  $\Sigma_0$ , in which we integrate the linearised equations for the dynamics of the heterogeneous perturbations. Dotted lines are contours of equal  $|\delta\dot{\gamma}|_{n=1}(t) = |\delta\dot{\gamma}|_{n=1}(0)2^M$  for integer  $M$  (We show only contours  $M > -50$ , thereby cutting off the final stage of the decay at the right hand side of the graph). The thick dashed line shows where the base state  $\partial_t^2 \dot{\gamma}_0 / \partial_t \dot{\gamma}_0 = 0$ , with linear instability to the left of it. The arrow denotes the stress value explored in detail in the insets (a)–(c). Parameters:  $\beta = 0.8$ ,  $\eta = 10^{-4}$ ,  $\tau_R = 0.0$ ,  $q = 0.1$ .

Figure 5(d) summarises the shear banding dynamics of the system across a range of stress values, in the plane of stress versus time. Any horizontal slice across this plane represents a single creep run at a constant value of the imposed stress  $\Sigma$ , as discussed in insets (a)–(c). The thick dashed line encloses to its left the regime of linear instability to the onset of banding, in which heterogeneous shear rate perturbations are predicted to grow. This line is obtained by applying our criterion (28) to the base state signal calculated numerically in a series of runs at closely spaced values of the imposed stress. To make an exploration of the dynamics of shear banding perturbations feasible in this full plane of stress versus time, we integrated the linearised equations of motion (26) (Performing the full non-linear and spatially aware simulation across a wide range of closely spaced stress values would be much more time consuming computationally.). The dotted lines show contours of equal  $|\delta\dot{\gamma}|_{n=1}(t) = |\delta\dot{\gamma}|_{n=1}(0)2^M$  for integer  $M$ . The region of growth in these perturbations agrees well with our analytical criterion enclosed by the dashed line. It corresponds to stress values  $0.61 \lesssim \Sigma \lesssim 0.75$  around the region of weakest slope of the constitutive curve.

Time-dependent shear banding during a sharp increase in the shear rate response  $\dot{\gamma}(t)$  following the imposition of a step stress has been reported experimentally in polymeric systems in [Boukany and Wang (2009a); Hu *et al.* (2007); Tapadia and Wang (2003); Hu *et al.* (2008); Boukany and Wang (2008); Hu and Lips (2005); Hu (2010); Boukany and Wang (2009c)].

The results in Fig. 5 apply to a system in which a heterogeneous perturbation is seeded once only, at the initial time  $t = 0$ . In practice, such a situation might correspond to the sample being left in a slightly heterogeneous state as a result of the experimental protocol by which it is initially loaded into the rheometer. Alternatively, perturbations may be seeded continuously during the experiment due to (for example) true thermal noise. To model this we also performed calculations in which small heterogeneous perturbations are added at every timestep. Pleasingly, we find qualitatively similar results: compare Figs. 5 and 6.



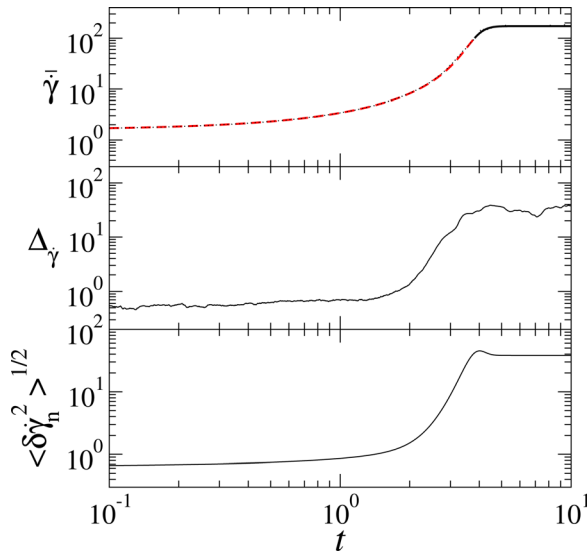
**FIG. 6.** Step stress in the RP model with noise added at each timestep. (a) Thick line: global shear rate  $\dot{\gamma}_0$  in a homogeneously constrained system, with the dashed region denoting  $\partial_t^2 \dot{\gamma}_0 / \partial \dot{\gamma}_0 > 0$ . Dotted line shows corresponding signal with heterogeneity allowed  $\bar{\dot{\gamma}}$ . (b) Degree of shear banding  $\Delta\dot{\gamma} = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}$  from a fully non-linear simulation with  $q = 0.1$  (Here a running average over data captured at frequent points in time is used, checked for qualitative convergence with respect to the capture frequency and running average range). (c) Shear rate perturbation  $\sqrt{\langle \delta\dot{\gamma}_n^2 \rangle}$  of the linearised system found by integrating Eq. (23). Magnitude of noise  $q = 10^{-5}$ . Values of model parameters are as in Fig. 5.

### C. Numerical results: Giesekus model

We now discuss our numerical results for an imposed step stress in the Giesekus model. To ensure a fair comparison with our study of the rolie-poly model just described, we use a value of the anisotropy parameter  $\alpha$  such that the underlying constitutive curve is monotonic and as closely resembling that of Fig. 3 as possible. Also as before, we set our value for the imposed stress to be in the region of weakest slope in this curve.

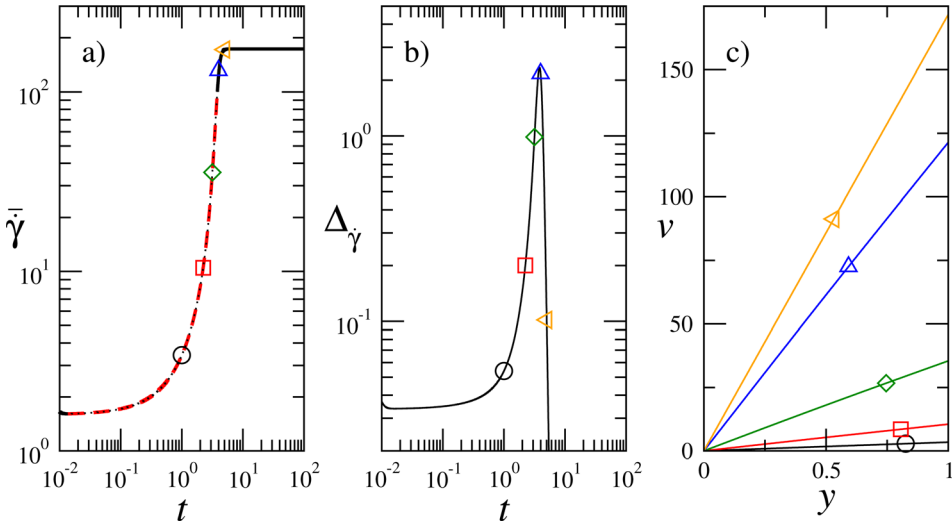
The shape of the shear rate response to this imposed step stress is qualitatively similar to that seen in the RP model, in particular in showing a regime of upward curvature [compare Figs. 6(a) and 7(a)]. In principle this upward curvature renders a state of initially homogeneous flow unstable to the development of shear bands. Indeed, shear rate heterogeneities do start to grow as a result of this linear instability. However we have never found them to grow sufficiently large as to give “significant” shear banding in our numerical simulations of the Giesekus model. The degree of banding  $\Delta\dot{\gamma}(t) = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}$  never exceeds 5% of the global shear rate  $\bar{\dot{\gamma}}(t)$  averaged across the sample, and thus would be hard to detect experimentally.<sup>1</sup> Contrast the results for  $\Delta\dot{\gamma}(t)$  and  $v(y)$  in Fig. 7 with their counterpart for the RP model in Fig. 5(c). By repeating this numerical calculation across a wide range of values of  $\alpha$ ,  $\eta$ , and  $\Sigma_0$ , we checked that this conclusion of negligible banding is general for this protocol in the Giesekus model.

The reason for this striking difference in shear banding behaviour between the two models, despite their differentiated creep response curves  $\dot{\gamma}_0(t)$  having the same upwardly curving shape, is that the maximal value of the curvature in  $\dot{\gamma}(t)$  is always much smaller in the



**FIG. 7.** Step stress in the Giesekus model. (a) Thick line: shear rate response in a homogeneously constrained system, with the dashed region denoting  $\partial_t^2 \dot{\gamma}_0 / \partial_t \dot{\gamma}_0 > 0$ . Dotted line shows corresponding signal with heterogeneity allowed, which is now indistinguishable from the homogeneous signal. (b) Degree of banding  $\Delta\dot{\gamma} = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}$ . (c) Snapshots of the velocity profile at times corresponding to symbols in (a) and (b). Parameters:  $\alpha = 0.6$ ,  $\eta = 10^{-3}$ ,  $\Sigma = 1.0$ ,  $q = 0.1$ .

<sup>1</sup>We note that, within the linear regime, the degree of banding  $\Delta\dot{\gamma}$  scales linearly with the magnitude of the initial noise  $q$ . Therefore, in order to make comparisons with the RP model the results presented in Secs. VB and VC have  $q = 0.1$ . We note that  $q$  values much larger than this are unrealistic for comparison to experiment.



**FIG. 8.** Step stress in the Giesekus model with parameters as in Fig. 7. Top: thick line shows the shear rate  $\dot{\gamma}_0$  in a homogeneously constrained system, with the dashed region denoting  $\partial_t^2 \dot{\gamma}_0 / \partial \dot{\gamma}_0 > 0$ . Dotted line shows corresponding signal with heterogeneity allowed  $\bar{\dot{\gamma}}$ , now indistinguishable from the homogeneous signal. Middle: degree of shear banding  $\Delta \dot{\gamma} = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}$  from the nonlinear simulation with  $q = 0.1$  (Here a running average over data captured at frequent points is used, checked for qualitative convergence with respect to the capture frequency and running average range). Bottom: shear rate perturbation  $\sqrt{\langle \delta \dot{\gamma}_{n=1}^2 \rangle}$  in linearised system found by integrating Eq. (23),  $q = 10^{-5}$ .

Giesekus model than the RP model [compare Figs. 5(a) and 7(a)]. Correspondingly, the resulting maximum degree of shear banding is much smaller.

In Fig. 7, heterogeneous perturbations are seeded once only, at the initial time  $t = 0$ . By comparison in Fig. 8 the system is first evolved to steady state at  $\Sigma = 0$  with small perturbations added at every timestep, before being evolved at the chosen  $\Sigma = \Sigma_0$  with perturbations again added continuously at every timestep. Although we never found “significant banding” ( $> 5\%$ ) in the Giesekus model with this noise history either, there is nonetheless an interesting feature not seen in the RP model. In particular, the amplitude of heterogeneity in steady flow is much greater than in the unsheared system at rest (In contrast, in the RP model the magnitude of heterogeneity in steady shear is comparable to that in zero shear, recall Fig. 6.) Whether or not these fluctuations would be large enough to be detected by sensitive velocimetry, this remains an interesting feature of the Giesekus model.

## VI. RESULTS: STRAIN RAMP

In this section we consider a strain ramp protocol in which a previously undeformed sample is subject to an applied shear at rate  $\dot{\gamma}_0$  by moving the top plate at speed  $\dot{\gamma}_0 L$  for times  $0 < t < t^*$ . After this the plate is held fixed, giving a total applied strain amplitude  $\gamma^* = \dot{\gamma}_0 t^*$ . The limit  $\dot{\gamma}_0 \rightarrow \infty$ ,  $t^* \rightarrow 0$  at fixed  $\gamma^*$  gives a theoretically idealised step strain. We focus here on ramp rates that are finite but nonetheless always fast compared to the terminal relaxation time. Therefore we impose  $\dot{\gamma}_0 \tau_d \gg 1$  in the RP model and  $\dot{\gamma}_0 \lambda \gg 1$  in the Giesekus model (For the RP model, we then separately distinguish between ramps for which  $\dot{\gamma}_0 \tau_R \ll 1$  and  $\dot{\gamma}_0 \tau_R \gg 1$ ). Following such fast ramps, we develop a criterion for the transient appearance of shear bands as the system relaxes back to equilibrium post-ramp.



### A. Criterion for instability after a fast strain ramp

We start by writing our general governing Eqs. (16) and (17) in a form that emphasizes the additive loading and relaxation dynamics that obtain in all constitutive equations of which we are aware

$$\Sigma(t) = G\mathbf{p} \cdot \mathbf{s}(y, t) + \eta \dot{\gamma}(y, t), \quad (29)$$

$$\partial_t \mathbf{s} = \dot{\gamma} \mathbf{S}(\mathbf{s}) - \frac{1}{\tau} \mathbf{R}(\mathbf{s}). \quad (30)$$

Here  $\tau$  is the terminal relaxation time (Two relaxation times, as in the sRP model, are included in this notation by writing  $\mathbf{R} = \mathbf{R}_1 + \frac{\tau}{\tau_R} \mathbf{R}_2$ ). For the purposes of the linear stability calculation that follows we have neglected small diffusive terms in Eq. (30), as discussed above.

To develop our criterion for the onset of shear banding we follow our usual linear stability procedure of considering an underlying base state of initially homogeneous flow response to the imposed deformation, and the dynamics of heterogeneous perturbations to this base state that might grow into observable shear banding. Accordingly we substitute perturbed fields as in Eq. (18) into the governing Eqs. (29) and (30), and expand in successive powers of the amplitude of the perturbations.

The zeroth order equations in this expansion govern the evolution of the base state. During the ramp this evolves according to

$$\begin{aligned} \frac{d\mathbf{s}_0}{d\gamma_0} &= \mathbf{S}(\mathbf{s}_0) - \frac{1}{\tau \dot{\gamma}_0} \mathbf{R}(\mathbf{s}_0), \\ &\approx \mathbf{S}(\mathbf{s}_0), \end{aligned} \quad (31)$$

in which we have divided the equation for the time-evolution of  $\mathbf{s}_0$  across by the constant shear rate  $\dot{\gamma}_0$  to give an equation instead for the evolution of  $\mathbf{s}_0$  with strain. In the second line we have specialised to the fast ramps of interest here, for which the loading dynamics dominates. Denoting the base state immediately as the ramp ends  $\mathbf{s}_0(t = t^{*-}) = \mathbf{s}_0^*$ , the dynamics of the base state immediately prior to the end of the ramp obeys

$$\left. \frac{d\mathbf{s}_0}{d\gamma_0} \right|_{t^{*-}} = \mathbf{S}(\mathbf{s}_0^*). \quad (32)$$

Post-ramp ( $\dot{\gamma}_0 = 0$ ) the base state relaxes back to equilibrium according to

$$\frac{d\mathbf{s}_0}{dt} = -\frac{1}{\tau} \mathbf{R}(\mathbf{s}_0). \quad (33)$$

Having discussed the evolution of the underlying homogeneous base state we now turn to the linearised dynamics of the heterogeneous perturbations. These are specified by the first order equations in the amplitude expansion just discussed [recall Eqs. (21) and (22)]. Post-ramp, these perturbations obey

$$\begin{aligned} \frac{d\delta \mathbf{s}_n}{dt} &= \left[ -\frac{G}{\eta} \mathbf{S}(\mathbf{s}_0) \mathbf{p} - \frac{1}{\tau} \partial_s \mathbf{R}|_{\mathbf{s}_0} \right] \cdot \delta \mathbf{s}_n. \\ &\simeq -\frac{G}{\eta} \mathbf{S}(\mathbf{s}_0) \mathbf{p} \cdot \delta \mathbf{s}_n. \end{aligned} \quad (34)$$

The approximation on the second line is valid for small values of the Newtonian viscosity compared with the zero shear polymer viscosity,  $\eta \ll G\tau$ , which is a good approximation in most complex fluids. Because the base state  $s_0$  is continuous across the end of the ramp, it follows that *immediately* post-ramp the perturbations obey

$$\left. \frac{d\delta s_n}{dt} \right|_{t^{*+}} = -\frac{G}{\eta} S(s_0^*) \mathbf{p} \cdot \delta s_n. \quad (35)$$

Combining Eq. (32) for the dynamics of the base state immediately before the ramp ends with Eq. (35) for the dynamics of the heterogeneous perturbations immediately post-ramp, we get

$$\left. \frac{\delta s_n}{dt} \right|_{t^{*+}} = -\frac{G}{\eta} \left. \frac{ds_0}{d\gamma_0} \right|_{t^{*-}} \mathbf{p} \cdot \delta s_n. \quad (36)$$

Projecting out the first component of this equation using the operator  $\mathbf{p}$ , and appealing to the linearity of the force balance condition (29), it is easy to show finally that shear rate perturbations obey, immediately post-ramp

$$\left. \frac{\delta \dot{\gamma}_n}{dt} \right|_{t^{*+}} = -\frac{1}{\eta} \left. \frac{\partial \Sigma_0}{\partial \gamma_0} \right|_{t^{*-}} \delta \dot{\gamma}_n. \quad (37)$$

This important result tells us that, immediately after a strain ramp has ended, an initially homogeneous flow state will be linearly unstable to the onset of shear banding if the shear stress had been decreasing in strain immediately before the ramp ended

$$\left. \frac{\partial \Sigma_0}{\partial \gamma_0} \right|_{t^{*-}} < 0. \quad (38)$$

This is consistent with the original insight of [Marrucci and Grizzuti \(1983\)](#) in the context of the DE model.

As usual, this criterion is expressed as a condition on the shape of the stress signal of an underlying base state of homogeneous flow response to the applied deformation. By definition, this base state stress signal equals the globally measured one at least until any significant banding takes place. Accordingly Eq. (38) can also be applied directly to the experimentally measured stress signal (This assumes that no appreciable banding developed during the ramp itself, which is a good assumption for the fast finite-amplitude ramps of interest here: even if the flow technically becomes linearly unstable to banding during the ramp, there is insufficient time for heterogeneity to develop.).

## B. Numerical results: RP model

In Sec. [VIA](#), we developed a criterion for linear instability, immediately following a rapid strain ramp, to the onset of shear banding post-ramp. This criterion is expressed as a condition on the shape of the stress signal of an underlying base state of homogeneous flow response to the applied deformation, immediately as the ramp ends.

In Subsection [VIB 1](#), we shall present numerical results for this base state signal throughout the full duration of its evolution, both during and after ramp. We also present

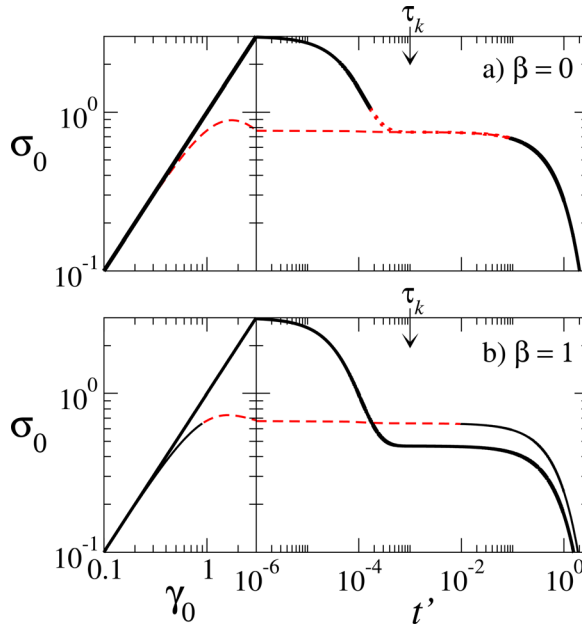
numerical results for any regions of linear stability (negative eigenvalues) or instability (positive eigenvalue) during this entire evolution. Recall that our analytically derived criterion (38) above strictly only applies immediately post-ramp. In Subsection VIB 2, we present the results of our spatially aware nonlinear simulations of the shear bands that arise as the result of any regimes of instability.

### 1. Base state and linear instability

Numerical results for the evolution of the base state stress signal, both during and after the ramp, are shown for the RP model in Fig. 9 (Here we have subtracted from  $\Sigma_0$  the trivial contribution  $\eta\dot{\gamma}_0$  from the Newtonian solvent to leave the viscoelastic contribution  $\sigma_0$  only.). For clarity it is plotted as a function of strain during the ramp, and of time afterwards. Regimes of linear instability to shear banding, determined by numerically calculating the time-dependent eigenvalue of the linearised equations discussed above, are shown as dotted and dashed lines. Consistent with our criterion (38) above, ramps that end with declining stress leave the system unstable immediately post-ramp.

With this figure in mind, we discuss now in more detail separately ramps that are slower and faster than the rate of stretch relaxation  $\tau_R^{-1}$  (As noted above, in each case the ramp is faster than the inverse terminal relaxation time,  $\dot{\gamma}_0\tau_d \gg 1$ ).

Consider first a “slow” ramp at a rate  $\dot{\gamma}_{0,n}$  for which  $\dot{\gamma}_{0,n}\tau_R \ll 1$ . For such a ramp, no appreciable chain stretch develops: subscript “n” denotes nonstretching. The ramp is still nonetheless in the fast flow regime  $\dot{\gamma}\tau_d \gg 1$  of the non-stretching version of the model specified by Eq. (14) above. The corresponding mechanical response during the ramp can then be computed by integrating only the terms prefactored by  $\dot{\gamma}$  in Eq. (14): it is effectively that of a nonlinear elastic solid with a stress signal that depends only on strain



**FIG. 9.** Viscoelastic contribution to the shear stress in the RP model during (vs  $\gamma_0$ ) and after (vs  $t'$ ) a strain ramp of amplitude  $\gamma^* = 3$ , with homogeneity enforced. (a)  $\beta = 0$  (no CCR), (b)  $\beta = 1$  (CCR active). Dotted/dashed lines denote linearly unstable regions ( $\omega > 0$ ). Upper curve at the end of each ramp is for a ramp rate  $\dot{\gamma}_{0,s}$  in the regime of chain stretch. Lower curve at the end of each ramp is for a ramp rate  $\dot{\gamma}_{0,n} = 500$  in the non-stretch regime. Parameters:  $\tau_R = 10^{-4}$ ,  $\eta = 10^{-5}$ ,  $\tau_k = 10\tau_R$ .

$\Sigma_0 = \Sigma_0(\gamma_0)$ , independent of strain-rate. Numerical results for this are shown by the lower of the two curves (during the ramp) in each panel of Fig. 9. It displays an overshoot at an amplitude  $\gamma_0 \sim 1.7$ . The system is therefore left unstable immediately post-ramp, as indicated by the red dashed lines, consistent with our criterion (38).

Post-ramp the base state stress signal shows mono-exponential decay on the single reptation timescale  $\tau_d$  of tube reorientation, as the system relaxes back to equilibrium. Allied to this, the eigenvalue of the stability analysis shows monotonic decay from its initial value towards a final value  $-(\frac{1}{\tau_d} + \frac{1}{\eta})$  which, being negative, indicates stability of the final homogeneous equilibrium state, as expected. Any system left linearly stable immediately post-ramp, by a ramp of amplitude  $\gamma_0 < 1.7$ , will therefore remain stable for all subsequent times and exhibit no banding (This case is not shown in the figure.). In contrast, a system that is left linearly unstable immediately post-ramp by a ramp of amplitude  $\gamma_0 > 1.7$ , returns finally to a stable homogeneous state (See again the lower curve at the end of the ramp in each panel of Fig. 9.). However shear bands do transiently form during the relaxation process, as we shall discuss in more detail in Subsection VIB 2.

Having discussed “slow” ramps with  $\dot{\gamma}_{0,n}\tau_R \ll 1$ , we now address “fast” ramps of typical rate  $\dot{\gamma}_{0,s}$  such that  $\dot{\gamma}_{0,s}\tau_R \gg 1$ . Here appreciable chain stretch develops during the ramp (Subscript “s” denotes stretching.). The associated mechanical response during the ramp then follows by integrating the terms in  $\dot{\gamma}$  in the sRP model Eq. (13). It again corresponds to that of an elastic solid, independent of strain-rate in this limit. Indeed because of the simple linear structure of the  $\dot{\gamma}$  terms in the sRP model, we now have a monotonically increasing relation  $\sigma_0 = G\gamma_0$ . The system is therefore left linearly stable against banding immediately post-ramp, as seen in the upper curve at the end of the ramp in each panel of Fig. 9, and consistent with our analytical criterion (38).

However it is important to recall that our analytically derived criterion (38) applies only *immediately* post-ramp and does not prescribe the system’s stability properties throughout the full duration of its relaxation back to equilibrium post-ramp. As seen in the upper curve (at the end of each ramp) in each panel of Fig. 9, this relaxation after a ramp of rate  $\dot{\gamma}_{0,s} \gg 1$  shows a double exponential form: first as chain stretch relaxes on the fast timescale  $\tau_R$ , and subsequently as tube reorientation takes place on the much slower reptation timescale  $\tau_d$ .

Insets (a) and (b), respectively, address a system without ( $\beta = 0$ ) and with ( $\beta = 1$ ) the CCR mechanism active. Immediately striking is the fact that, without CCR [inset (a)] the first part of the stress relaxation on the fast timescale of stretch relaxation  $\tau_R$ , returns the stress to a value equal to that which would have been generated by a ramp of equivalent amplitude in the slower non-stretching limit: the upper curve in inset (a) rejoins the lower one on an intermediate plateau around the time  $\tau_k = 10\tau_R$ , before both finally follow the same decay on the terminal timescale  $\tau_d$ . Denoting by  $\sigma(t' = \tau_k, \dot{\gamma}_0, \gamma_0)$  the stress on this intermediate plateau, then, for a ramp of amplitude  $\gamma_0$  we have

$$\sigma(\tau_k, \dot{\gamma}_{0,s}, \gamma_0) = \sigma(\tau_k, \dot{\gamma}_{0,n}, \gamma_0) \quad \text{for } \beta = 0. \quad (39)$$

Once this intermediate plateau has been attained, the stability properties of the two curves in Fig. 9(a) coincide. Following a fast ramp of rate  $\dot{\gamma}_{0,s}$  and amplitude  $\gamma_0 > 1.7$ , therefore, we predict a *delayed* banding instability that sets in a time  $O(\tau_R)$  post-ramp, even though no stress overshoot occurred during the ramp itself. This will be confirmed by our spatially aware simulation showing shear banding in Subsection VIB 2. It is consistent with experimental results that show delayed shear banding setting in on a timescale  $O(\tau_R)$  post-ramp [Boukany *et al.* (2009); Archer *et al.* (1995)].

In contrast, with CCR active ( $\beta \neq 0$ ) the stress remaining after the initial part of the stress decay on the fast timescale  $\tau_R$  is significantly lower than that which would have

been generated by a ramp of corresponding amplitude in the slower, non-stretching regime: the intermediate plateau values do not coincide in Fig. 9(b). Indeed, for large enough  $\beta$  this initial fast relaxation is sufficient to ensure that the system remains stable against the formation of bands throughout the full duration of its return to equilibrium, as seen in Fig. 9(b). We therefore conclude that in order to observe shear banding after a ramp in the chain stretching regime, the value of the CCR parameter  $\beta$  should be small  $\beta \sim 0$ .

These differences in the system's relaxation properties with and without CCR can be explained as follows. Without CCR ( $\beta = 0$ ), the mechanisms of chain stretch relaxation and tube orientation relaxation are decoupled and occur independently of each other. The residual stress remaining after chain stretch has relaxed following a “fast” ramp of rate  $\dot{\gamma}_{0,s}$  is therefore equal to the stress that would have resulted from a ramp of the same amplitude but rate  $\dot{\gamma}_{0,n}$  during which no chain stretch arose in the first place. In contrast, with CCR ( $\beta \neq 0$ ) the relaxation of chain stretch also brings significant relaxation in the orientation of tube segments, because a proportion of the entanglements forming the tube of constraints on a test chain are lost upon stretch relaxation. The stress relaxation is thereby accelerated for times  $t' < \tau_R$  compared with the non-CCR case (We note that the constitutive curves are non-monotonic or monotonic for  $\beta = 0$  or 1 [respectively, with  $\eta = 10^{-5}$ ]. However, the non-monotonicity of the steady state constitutive curve is not directly related to the phenomenon discussed here, which concerns relaxation after ramps that do not last long enough to probe the steady state of shear flow.).

## 2. Nonlinear, spatially aware simulations

So far, we have discussed the evolution of the base state stress during and after a strain ramp, and its associated time-dependent linear stability properties. We now perform non-linear simulations to investigate the shear bands that form as a result of any regime of linear instability.

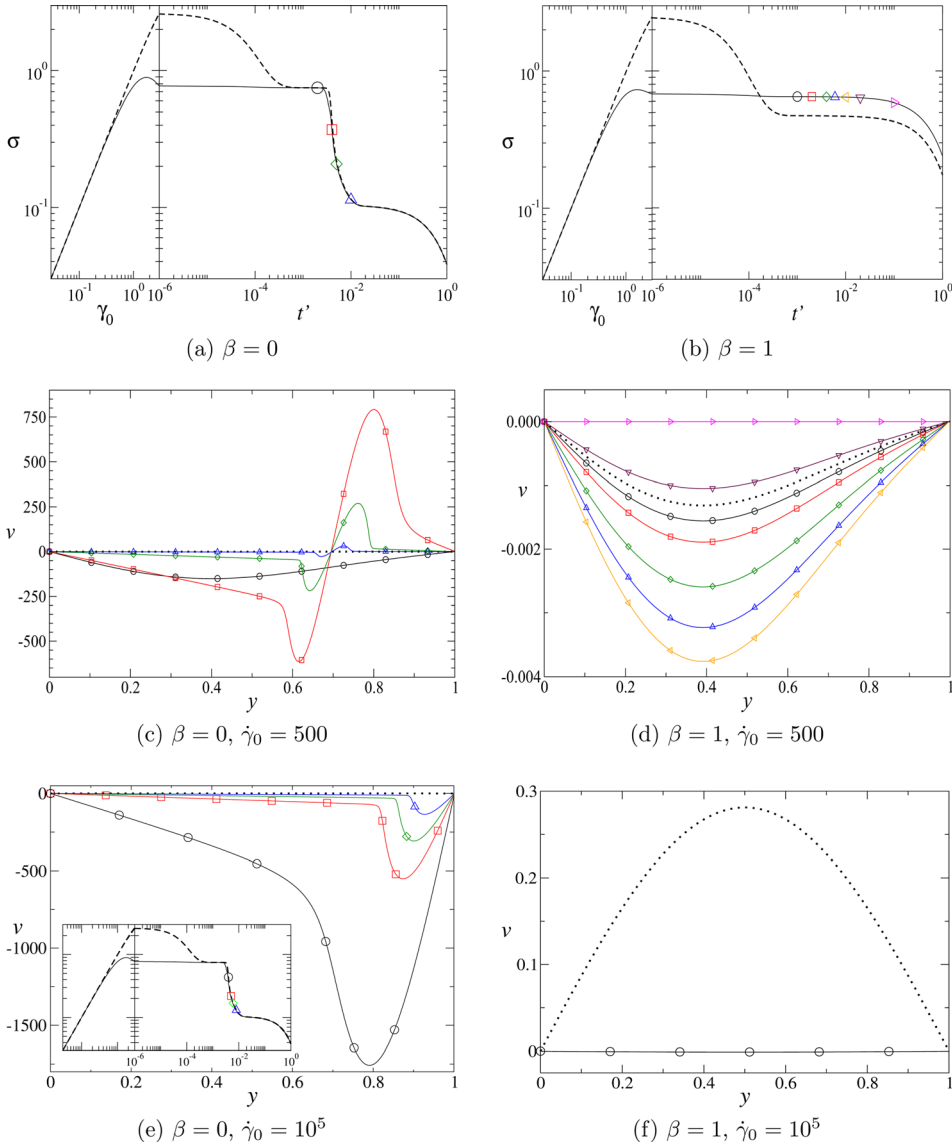
As can be seen in Fig. 10 the results are consistent with our linear instability predictions of Fig. 9. Insets (c) and (d) show that shear rate perturbations grow as soon as a ramp of rate  $\dot{\gamma}_{0,n}$  and amplitude  $\gamma_0 > 1.7$  ends. For example, appreciable heterogeneity has already developed by the time indicated by the circle in (a). In contrast, insets (e) and (f) show that after a “fast” ramp of rate  $\dot{\gamma}_{0,s}$  and amplitude  $\gamma_0 > 1.7$ , the system shows onset of shear rate heterogeneity only after a delay time  $t' \sim \tau_k$ , and only for systems in which CCR is sufficiently small  $\beta \sim 0$  [inset (e)]. With CCR active [inset (f)] any residual heterogeneity at the end of the ramp decays monotonically.

Figure 10(a) also demonstrates that shear rate heterogeneity of the large magnitude seen in this protocol can dramatically alter the stress relaxation function. As the local shear rate becomes extremely large, nonlinearities become important and result in a sudden and dramatic acceleration of stress relaxation compared with the base state signal of Fig. 9. This causes the second drop-off in stress in that inset (recall that the first drop-off after the fast ramp in contrast arose from chain stretch relaxation in the underlying base state).

## C. Comparison with experiment

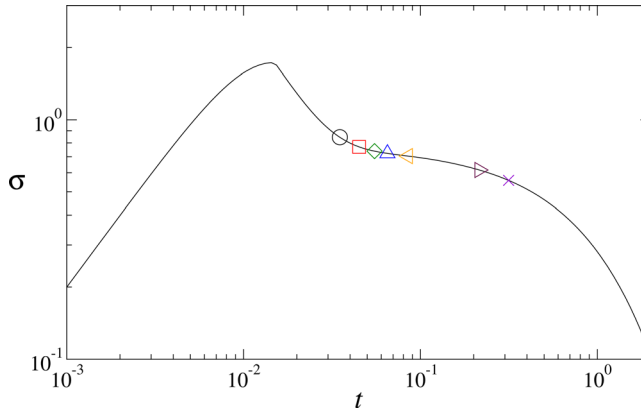
We now discuss our results in relation to experimental observations of shear banding following the imposition of a fast strain ramp in polymeric fluids. In doing so, we recall that shear banding is often described as “macroscopic motions” in the context of this protocol.

For strain ramps that terminate in a regime of declining stress versus strain, macroscopic motions accompanied by a dramatic drop in the stress signal were reported to develop quickly post-ramp by Boukany and Wang (2008, 2009b). This is consistent with our analytical criterion (38), and also with our numerics in Figs. 10(c) and 10(d).



**FIG. 10.** Strain ramp in the RP model. (a) Shear stress during (vs  $\gamma_0$ ) and after (vs  $t'$ ) a ramp of amplitude  $\gamma^* = 3$ , with CCR inactive,  $\beta = 0$ . The dashed line is for a ramp of fast rate  $\dot{\gamma}_{0,s} = 10^5$  in the chain stretching regime; the solid line is for a ramp of rate  $\dot{\gamma}_{0,n} = 500$  in the non-stretching regime. (b) Corresponding curves with CCR active,  $\beta = 1$ . (c), (d) Velocity profiles during stress relaxation at times corresponding to symbols in (a) and (b), respectively, in both cases following a ramp of rate in the non-stretching regime  $\dot{\gamma}_{0,n} = 500$ . Corresponding (e) and (f) are for a ramp of fast rate  $\dot{\gamma}_{0,s} = 10^5$  in the stretching regime. Profiles are shown at times corresponding to symbols in the inset for (e) and at times corresponding to symbols in (b) for (f). The normalised velocity heterogeneity  $v_0(y) = v(y) - \dot{\gamma}_0 y$  immediately before the end of the ramp at  $t = t^{*-}$  is shown as a thick dotted line. Model parameters  $\tau_R = 10^{-4}$ ,  $\eta = 10^{-5}$ . Initial noise magnitude  $q = 5 \times 10^{-4}$ .

For strain ramps of amplitudes  $\gamma_0 \gtrsim 1.5$  that show no stress overshoot during the ramp, delayed macroscopic motions have been reported post-ramp in polymer melts [Boukany *et al.* (2009); Boukany and Wang (2009b)] and solutions [Archer *et al.* (1995)]. These onset after a time  $t' = O(\tau_R)$  and are concurrent with a sudden drop in the stress signal. These observations are consistent with the stress response and associated

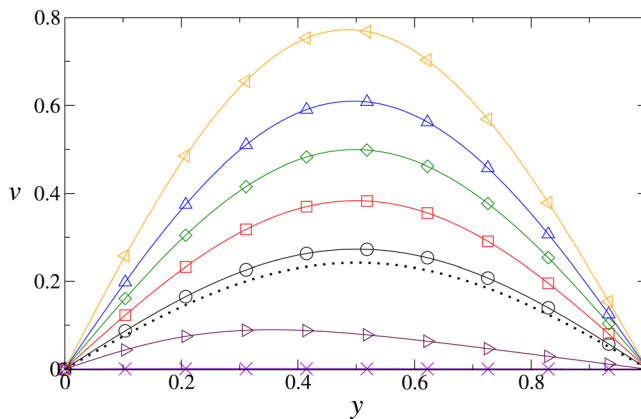


**FIG. 11.** Viscoelastic stress during and after a strain ramp of amplitude  $\gamma_0 = 3$  and rate  $\dot{\gamma}_0 = 200$ ; time of shear cessation  $t^* = 0.015$ . Here  $\tau_R = 10^{-2}$ ,  $\eta = 10^{-5}$ ,  $\beta = 0$ , and initial noise magnitude  $q = 10^{-2}$ .

transient shear banding in the RP model for  $\beta \sim 0$  following a strain ramp of rate  $\dot{\gamma}_{0,s}$  and amplitude  $\gamma_0 \geq 1.7$  [recall Fig. 10(e)].

Experimental reports of similar macroscopic motions but without the accompanying dramatic drop in the stress signal post-ramp are also widespread [Wang *et al.* (2006); Fang *et al.* (2011); Boukany *et al.* (2009); Li and Wang (2010); Ravindranath *et al.* (2011); Ravindranath and Wang (2007)]. Qualitatively similar behaviour can be uncovered in the RP model by decreasing the entanglement number  $Z$  to give less well separated relaxation timescales  $\tau_d, \tau_R$ . This decreases the maximal degree of banding observed post-ramp to a sufficient extent that the global stress signal no longer differs significantly from that of the homogeneous constrained system. An example of such behaviour is shown in Figs. 11 and 12. The stress signal now shows a single drop-off associated with chain stretch relaxation, but lacks a second drop-off associated with the nonlinear effects of banding.

Indeed, our numerical runs in Figs. 9 and 10 assumed an entanglement number  $Z = 3300$  larger than is the case experimentally. We set this number deliberately to ensure a clean separation of timescales  $\tau_d = 10^4 \tau_R$ , thereby allowing a clear pedagogical discussion of the relative effects of the relaxation of chain stretch and the relaxation of tube orientation post-ramp.



**FIG. 12.** Snapshots of the velocity profile during stress relaxation after a ramp shown in Fig. 11, at times corresponding to symbols in that figure. Dotted line: snapshot of the normalised velocity profile  $v_0(y) = v(y) - \dot{\gamma}_0 y$  at time  $t = t^*$ .



In practice, however, polymer melts with  $Z \geq 100$ , and DNA or wormlike micelles with  $Z \geq 150$ , usually suffer edge fracture so that reliable results are difficult to obtain. The separation of time scales in experiment is therefore more typically  $\tau_d/\tau_R \sim 150 - 500$ . Upon repeating our simulations for these more realistic values of  $\tau_d/\tau_R$ , and for less severe ramp rates  $\dot{\gamma}_{0,s}$ , we find, reassuringly, that the qualitative features described above still obtain (provided  $\tau_d/\tau_R \geq 10$  and  $\dot{\gamma}_{0,s} > \tau_R^{-1}$ ) (see Figs. 11 and 12). We do not attempt to reproduce specific experimental results by matching the relaxation times or ramp rates in detail in this work, because studies elsewhere have done so [Agimelen and Olmsted (2013); Agimelen (2012)].

Finally, we comment on our numerical findings in relation to the A, B, C classification system discussed in Sec. II. As seen towards the right hand side of Fig. 10, the development of very large local shear rates post-ramp is closely associated with a stress relaxation that is accelerated compared with that which would be predicted by a calculation in which homogeneity is imposed by assumption. This can result in a significant decrease in the damping function compared with that predicted by any homogeneous calculation and so to type C behaviour. Conversely, for systems in which the macroscopic motions that develop are more modest (even if still observable experimentally), the stress relaxation function agrees well with that of a calculation in which homogeneity is assumed, leading to a damping function of type A.

Furthermore, a decreasing separation of relaxation times  $\tau_d/\tau_R$  (decreasing entanglement number  $Z$ ) causes the maximal degree of banding to decrease and so could lead correspondingly to a progression from type C to type A behaviour. This is consistent with reports that type C behaviour is most common in very well entangled polymers, while type A behaviour occurs most often for moderately entangled polymers [Venerus (2005); Osaki (1993)]. We conclude that the RP model is capable of exhibiting both types A and C behaviour, with a progression between the two consistent with that seen experimentally. To the best of our knowledge, the RP model is unable to show the less commonly reported type B behaviour of very weakly entangled materials [Venerus (2005); Osaki (1993)]. Indeed, the RP model is in any case not aimed at describing these systems.

We note finally that the Giesekus model has a linear stress-strain relation in a fast strain ramp protocol:  $\Sigma \sim G\gamma$ . It therefore predicts linear stability against shear banding immediately after a fast strain ramp, according to Eq. (38). Furthermore this model contains only one relaxation time. Accordingly it is unlikely to capture the rich experimental phenomenology just discussed for this protocol, and we do not discuss it further here.

## VII. RESULTS: SHEAR STARTUP

We consider finally the shear startup protocol, in which a previously well rested sample is subject to shearing at a constant rate  $\dot{\gamma}_0$  for all times  $t > 0$ , giving a strain  $\gamma_0 = \dot{\gamma}_0 t$ . We first derive an analytical criterion for the onset of banding in this protocol, before presenting numerical results that support it.

### A. Criterion for instability in shear startup

In a shear startup experiment, the most commonly reported rheological response function is that of the startup stress as a function of time  $t$ , or equivalently as a function of strain  $\gamma_0 = \dot{\gamma}_0 t$ , for the given applied strain-rate  $\dot{\gamma}_0$ . When plotted as a function of accumulated strain  $\gamma_0$  for a collection of startup runs, each performed at a constant value of the strain-rate  $\dot{\gamma}_0$ , this gives us a two-dimensional function  $\Sigma_0(\gamma_0, \dot{\gamma}_0)$ .

In the context of shear banding, a familiar thought-experiment is to consider an (artificial) situation in which a startup flow is constrained to remain homogeneous until the

system attains a stationary state in the limit  $\gamma_0 \rightarrow \infty$ . In this limit, the total accumulated strain becomes irrelevant and the stress depends only on strain-rate:  $\Sigma_0 = \Sigma_0(\dot{\gamma}_0)$ . The criterion for shear banding (with the constraint now removed) is well known in this limit: that the underlying constitutive curve of stress as a function of strain-rate has negative slope,  $d\Sigma_0/d\dot{\gamma}_0 < 0$ .

Our aim here is to generalise this result, which is valid only for a stationary homogeneous base state in the limit  $\gamma_0 \rightarrow \infty$ , to finite strains  $\gamma_0$  and times  $t$ , in order to predict at what stage during startup banding first sets in. As we shall show, the onset of banding is closely associated with the time (or equivalent strain) of any overshoot in the stress startup signal  $\Sigma_0(\gamma_0)$ , for a given applied strain-rate  $\dot{\gamma}_0$ . Clearly this implies an onset criterion  $d\Sigma_0/d\gamma_0 < 0$ , which is indeed a very useful rule of thumb to apply to experimental data. However we show below that it is in fact modified slightly, leading to onset a little before overshoot.

Besides predicting the time at which bands first start to form in any experiment for which the eventual steady state is banded,  $d\Sigma_0/d\dot{\gamma}_0 < 0$ , an important further outcome of what follows will be to predict the transient appearance of shear bands, again associated with a startup overshoot and subsequently declining stress  $d\Sigma_0/d\gamma_0 < 0$ , even in systems for which the underlying constitutive curve is monotonic  $d\Sigma_0/d\dot{\gamma}_0 > 0$  and the steady state unbanded.

As ever, our strategy will be to consider an underlying base state of initially homogeneous flow response, and the dynamics of small heterogeneous perturbations about it. Our criterion for the growth of these perturbations, i.e., for the onset of banding, will be expressed in terms of the partial derivatives of the base state stress signal  $\Sigma_0(\gamma_0, \dot{\gamma}_0)$  with respect to  $\gamma_0$  and  $\dot{\gamma}_0$ .

In many places below we shall graphically present results in the plane of  $\gamma_0$  and  $\dot{\gamma}_0$ . To interpret data presented in this way, it is useful to keep in mind that a vertical cut up this plane at its far right hand side  $\gamma_0 \rightarrow \infty$  corresponds to the system's steady state properties as a function of strain-rate  $\dot{\gamma}_0$ . A horizontal cut corresponds to the system's startup behaviour as a function of accumulated strain  $\gamma_0$ , in a single startup run performed at a fixed value of the strain-rate  $\dot{\gamma}_0$ .

As noted in the context of the other protocols above, because the base state signal corresponds to the experimentally measured one at least until appreciable banding develops, the criterion that we develop can be applied directly to experimentally measured stress startup data.

To start, then, we consider the properties of an underlying base state of initially homogeneous flow response to an imposed shear startup deformation. Were the flow to remain homogeneous through to the stationary limit  $\gamma_0 \rightarrow \infty$ , the condition for banding instability would then be that the stationary constitutive curve of stress as a function of strain-rate has a region of negative slope  $d\Sigma_0/d\dot{\gamma}_0 < 0$ , as noted above. In practice, however, the flow generally becomes unstable to banding before this stationary limit is attained. As a first step to generalising our onset criterion to finite strains during startup, we define a fixed-strain constitutive curve

$$\Sigma_0(\dot{\gamma}_0)|_{\gamma_0=\text{const.}} = GW_{xy0}(\dot{\gamma}_0)|_{\gamma_0=\text{const.}} + \eta\dot{\gamma}_0. \quad (40)$$

Experimentally, such a curve would be constructed by performing a series of startup runs at different shear rates and plotting the shear stress, grabbed at the same fixed-strain  $\gamma_0$  in each run, as a function of the applied shear rate.

We then consider the derivative of this fixed-strain constitutive curve with respect to shear rate

$$\partial_{\dot{\gamma}_0} \Sigma_0|_{\gamma_0} = G \partial_{\dot{\gamma}_0} W_{xy_0}|_{\gamma_0} + \eta. \quad (41)$$

This clearly reduces to the slope of the underlying steady state constitutive curve  $d\Sigma_0/d\dot{\gamma}_0$  in the limit  $\gamma_0 \rightarrow \infty$ , and more generally is the finite-strain analogue of it.

To proceed further, we need an expression for  $\partial_{\dot{\gamma}_0} W_{xy_0}|_{\gamma_0}$ . To obtain this we return to Eq. (17) divided across by strain-rate

$$\partial_{\dot{\gamma}_0} \mathbf{s}_0|_{\dot{\gamma}_0} = \frac{1}{\dot{\gamma}_0} \mathbf{Q}(\mathbf{s}_0, \dot{\gamma}_0). \quad (42)$$

We again neglect diffusive terms, which are small for the most unstable mode in the linear regime. Differentiating this with respect to strain-rate gives

$$\partial_{\dot{\gamma}_0} \partial_{\dot{\gamma}_0} \mathbf{s}_0 = -\frac{1}{\dot{\gamma}_0} \partial_{\dot{\gamma}_0} \mathbf{s}_0|_{\dot{\gamma}_0} + \frac{1}{\dot{\gamma}_0} \mathbf{M} \cdot \partial_{\dot{\gamma}_0} \mathbf{s}_0|_{\dot{\gamma}_0} + \frac{1}{\dot{\gamma}_0} \mathbf{q}, \quad (43)$$

in which  $\mathbf{M} = \partial_s \mathbf{Q}|_{\mathbf{s}_0, \dot{\gamma}_0}$  and  $\mathbf{q} = \partial_{\dot{\gamma}} \mathbf{Q}|_{\mathbf{s}_0, \dot{\gamma}_0}$ , as previously. Multiplying by  $\dot{\gamma}_0 \mathbf{M}^{-1}$  and rearranging we have

$$\partial_{\dot{\gamma}_0} \mathbf{s}_0|_{\dot{\gamma}_0} = \mathbf{M}^{-1} \cdot (\partial_{\dot{\gamma}_0} \mathbf{s}_0|_{\dot{\gamma}_0} - \mathbf{q} + \dot{\gamma}_0 \partial_{\dot{\gamma}_0} \partial_{\dot{\gamma}_0} \mathbf{s}_0). \quad (44)$$

Using  $\mathbf{p}$  to project out the first component gives

$$\partial_{\dot{\gamma}_0} W_{xy_0}|_{\dot{\gamma}_0} = \mathbf{p} \cdot \mathbf{M}^{-1} \cdot (\partial_{\dot{\gamma}_0} \mathbf{s}_0|_{\dot{\gamma}_0} - \mathbf{q} + \dot{\gamma}_0 \partial_{\dot{\gamma}_0} \partial_{\dot{\gamma}_0} \mathbf{s}_0), \quad (45)$$

which, substituted into Eq. (41), gives finally an expression

$$\partial_{\dot{\gamma}_0} \Sigma_0|_{\dot{\gamma}_0} = G \mathbf{p} \cdot \mathbf{M}^{-1} (\partial_{\dot{\gamma}_0} \mathbf{s}_0|_{\dot{\gamma}_0} - \mathbf{q} + \dot{\gamma}_0 \partial_{\dot{\gamma}_0} \partial_{\dot{\gamma}_0} \mathbf{s}_0) + \eta, \quad (46)$$

for the derivative with respect to shear rate of the fixed-strain constitutive curve of the underlying homogeneous base state. We shall return to this expression in a few lines below.

We now turn to consider the dynamics of any heterogeneous perturbations to the homogeneous base state just discussed. Recalling Eqs. (21) and (22), we have

$$\partial_t \delta \mathbf{s}_n = \left( \mathbf{M} - \frac{G}{\eta} \mathbf{q} \mathbf{p} \right) \cdot \delta \mathbf{s}_n. \quad (47)$$

The criterion for this system of linear equations to have a positive eigenvalue, which signifies onset of instability to the growth of shear banding perturbations at any time, is

$$(-1)^D \left| \mathbf{M} - \frac{G}{\eta} \mathbf{q} \mathbf{p} \right| > 0, \quad (48)$$

where  $D$  is the dimensionality of  $\mathbf{M}$  (We neglect the possibility of the emergence of two complex conjugate eigenvalues of positive real part—a Hopf bifurcation—because we have never seen this in practice in our numerics.). This corresponds exactly to

$$(-1)^D |\mathbf{M}| \left( 1 - \frac{G}{\eta} \mathbf{p} \cdot \mathbf{M}^{-1} \cdot \mathbf{q} \right) > 0. \quad (49)$$

Using the fact that  $(-1)^D |\mathbf{M}| < 0$  (which follows from noting that the base state must be stable with respect to *homogeneous* perturbations at fixed  $\dot{\gamma}_0$ ), this further corresponds exactly to

$$\eta - G\mathbf{p} \cdot \mathbf{M}^{-1} \cdot \mathbf{q} < 0. \quad (50)$$

Combining this with Eq. (46) above for the base state, we find finally an exact criterion for the onset of a linear instability to shear banding during startup

$$\partial_{\dot{\gamma}_0} \Sigma_0|_{\dot{\gamma}_0} - G\mathbf{p} \cdot \mathbf{M}^{-1} \cdot (\partial_{\dot{\gamma}_0} \mathbf{s}_0|_{\dot{\gamma}_0} + \dot{\gamma}_0 \partial_{\dot{\gamma}_0} \partial_{\dot{\gamma}_0} \mathbf{s}_0) < 0. \quad (51)$$

In raw form, this criterion appears cumbersome and somewhat removed from conveniently measurable experimental quantities. However its overall structure is physically transparent. The first term is a derivative of the base state stress with respect to strain-rate. The second term is a derivative of the base state with respect to strain. The third is a cross term, containing derivatives with respect to both. To illuminate its physical content, therefore, we start by discussing two distinct and physically important limits in which the first and second terms separately dominate.

Consider first an (artificial) situation in which a homogeneous startup flow proceeds through to a stationary state in the limit of large strain  $\gamma_0 \rightarrow \infty$ , without banding en route. In this limit, derivatives with respect to strain  $\partial_{\dot{\gamma}}$  vanish from Eq. (51) and we recover the familiar, and much simpler, criterion for banding in steady state already discussed above

$$\partial \dot{\Sigma}_0|_{\gamma_0 \rightarrow \infty} < 0. \quad (52)$$

This criterion also applies (less artificially) to the onset of a linear instability to shear banding during an experiment in which the strain-rate  $\dot{\gamma}_0$  is slowly swept upwards from zero. Because the material is flowing in a liquid-like way in this limit, we term this a “viscous instability” for convenient nomenclature in what follows.

Consider conversely a single startup run performed in the limit of a very fast flow  $\dot{\gamma}_0 \rightarrow \infty$ . In this regime many viscoelastic materials behave essentially as elastic solids, with the stress startup function converging to a limiting curve  $\Sigma_0(\gamma_0)$  from which any dependence on shear rate is lost,  $\partial \dot{\gamma} \rightarrow 0$ . The full criterion (51) then reduces to

$$-G\mathbf{p} \cdot \mathbf{M}^{-1} \cdot \partial_{\dot{\gamma}_0} \mathbf{s}|_{\dot{\gamma}_0} < 0. \quad (53)$$

Because in this limit the material responds essentially as an elastic solid, we term this an “elastic instability” for convenient nomenclature in what follows. We underline that we adopt this terminology in this manuscript to mean the onset of a shear banding instability in a regime in which the material is behaving as an elastic solid (entirely distinct from elastic or viscoelastic Taylor-Couette instabilities or elastic turbulence discussed elsewhere in the literature [Larson *et al.* (1990)]).

Although simpler than Eq. (51), Eq. (53) is still not expressed in terms of quantities that are easily measured experimentally. However further simplification is possible in the case of only two dynamical variables  $D = 2$ , for example in flow regimes in which the dynamics is dominated by the shear stress and only one component of normal stress difference. In this case (53) further reduces to

$$-\frac{1}{\dot{\gamma}_0^2} \text{tr} \mathbf{M} \partial_{\dot{\gamma}_0} \Sigma_0|_{\dot{\gamma}_0} + \frac{1}{\dot{\gamma}_0} \partial_{\dot{\gamma}_0}^2 \Sigma_0|_{\dot{\gamma}_0} < 0 \quad \text{with} \quad \text{tr} \mathbf{M} < 0. \quad (54)$$

Taken alone, the first term of this expression predicts onset of banding immediately after any overshoot in the stress as a function of strain during startup. The second term modulates this result slightly, allowing onset slightly before overshoot, once the stress starts to curve downwards. This prediction is consistent with numerous experimental observations of time-dependent shear banding associated with stress overshoot during startup: in soft glassy materials [Divoux *et al.* (2010, 2011a); Martin and Hu (2012)] and entangled polymer melts and solutions [Ravindranath *et al.* (2008); Ravindranath and Wang (2008); Boukany and Wang (2009a); Tapadia and Wang (2006); Hu *et al.* (2007)], and also in simulation studies [Zhou *et al.* (2008); Adams and Olmsted (2009a, 2009b); Adams *et al.* (2011); Moorcroft *et al.* (2011); Cao and Likhtman (2012); Manning *et al.* (2007)].

## B. Numerical results: Rolie-poly model

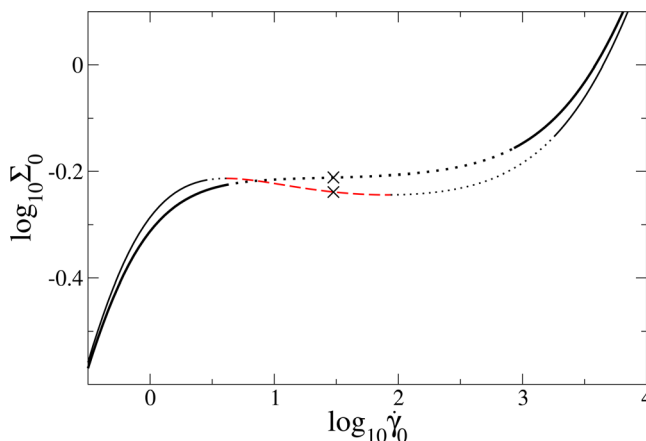
In this section, we present our numerical results for shear startup in the RP model. We consider first the limit in which polymer chain stretch is negligible,  $\dot{\gamma}_0 \tau_R \ll 1$ , before commenting on the effects of stretch.

The behaviour of the rolie-poly model in startup has been studied previously numerically by Adams *et al.* (2011, 2008). One of our aims in what follows is to understand the phenomena reported in that work, some of which we must necessarily reproduce in our numerics here, in the context of the general analytical criterion developed above.

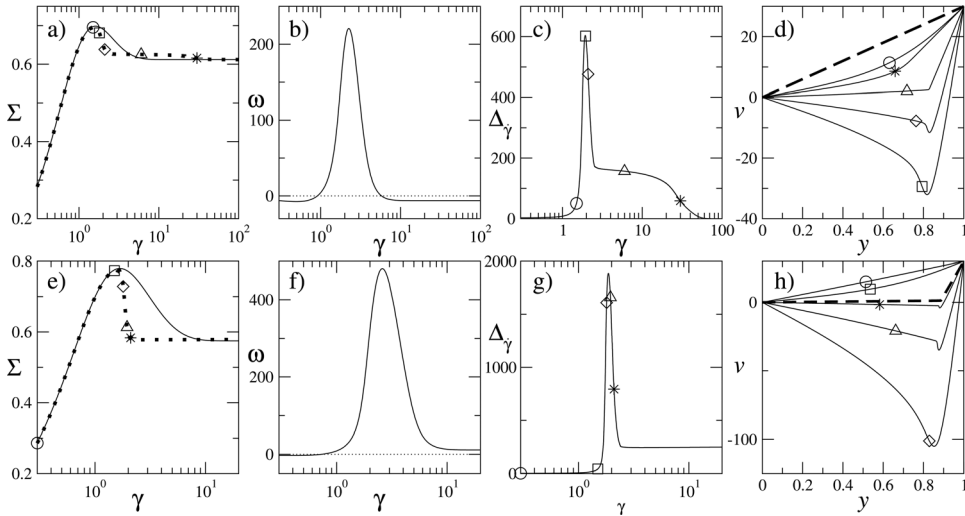
### 1. Nonstretching rolie-poly model

Depending on the values of the model parameters  $\beta, \eta$ , the underlying constitutive curve of the nRP model can either be monotonic or non-monotonic. A representative example of each case is shown in Fig. 13.

We consider first the non-monotonic case, for a shear rate indicated by the cross in the negatively sloping regime  $d\Sigma_0/d\dot{\gamma}_0 < 0$ . The model's shear startup behaviour at this imposed shear rate is explored in the bottom row of Fig. 14. The velocity profile shown by the thick dashed line in the bottom right inset shows that the steady flowing state is shear banded, consistent with a “viscous instability” implied by the negative slope  $d\Sigma_0/d\dot{\gamma}_0 < 0$  in the constitutive curve.



**FIG. 13.** Constitutive curves of the nRP model for  $\beta = 0.4, 1$  (bottom to top on the right) and  $\eta = 10^{-4}$ . Dashed: linearly unstable at steady state. Dotted: transiently linearly unstable before the steady state is reached. Crosses denote shear rate  $\dot{\gamma} = 30$  for which time-dependent shear startup behaviour is explored in Fig. 14.



**FIG. 14.** Responses of the nRP model to an imposed shear rate  $\dot{\gamma} = 30$  for the case of a monotonic constitutive curve  $\beta = 1$  (top row) and for the case of non-monotonic constitutive curve  $\beta = 0.4$  (bottom row). (a), (e) Shear stress response with homogeneity enforced (solid line) and with heterogeneity allowed (dotted line). (b), (f) Linear stability analysis results for the real part of the eigenvalue that has the largest real part. (c), (g) Degree of banding  $\Delta\dot{\gamma} = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}$  in full nonlinear simulations. (d), (h) Snapshots of the velocity profile at strains corresponding to symbols in (a)/(c), (e)/(g). Steady state velocity profile is shown as a thick dashed line.  $\eta = 10^{-4}$ ,  $q = 0.1$ .

Also immediately obvious in Fig. 14 is the fact that bands first form rather early during the startup process, apparently triggered by an “elastic instability” associated with the startup stress overshoot and subsequently declining stress  $d\Sigma_0/d\gamma_0 < 0$ . When first formed these are much more pronounced than in steady state, as shown by the pronounced spike in the degree of banding  $\Delta\dot{\gamma}$ . Indeed this “elastic banding” can be so pronounced as to precipitate a negative local shear rate in the low shear band. This is consistent with the material in that band behaving effectively as an elastic solid because an elastic solid subject to a declining stress, as the stress falls from its peak overshoot value, must shear backwards. Depending on the duration and strength of that negative shear, this can even give rise to negative local velocities. In this way, the existence of a stress overshoot can be seen as a necessary but not sufficient condition for recoil. Clearly, then, in shear startup an “elastic instability” associated with stress overshoot can precede and be much more violent than any “viscous instability” associated with steady state banding.

For shear rates shown by the dotted lines either side of the negatively sloping regime  $d\Sigma_0/d\dot{\gamma}_0 < 0$  in Fig. 13, steady state “viscous instability” is absent, but a pronounced “elastic instability” can nonetheless still arise during startup. This leads to the formation of pronounced banding that persists only transiently, before decaying to leave homogeneous flow in steady state.

The model’s startup behaviour across a wide range of imposed shear rates  $\dot{\gamma}_0$  is summarised in Fig. 16. In the left panel of this figure we show our linear stability criteria for the onset of banding in the full plane of  $\dot{\gamma}_0, \gamma_0$ . As noted above, horizontal cut across this plane corresponds to the fluid’s startup behaviour as a function of accumulated strain, at a single fixed value of the strain-rate. A vertical cut at the far right hand side corresponds to the system’s steady state properties as a function of strain-rate. We again use parameter values for  $\beta, \eta$  corresponding to the non-monotonic constitutive curve in Fig. 13.

Accordingly, the startup run explored in the bottom row of Fig. 14 corresponds to horizontal slice through Fig. 15 at a fixed value of  $\dot{\gamma}_0 = 30$ .

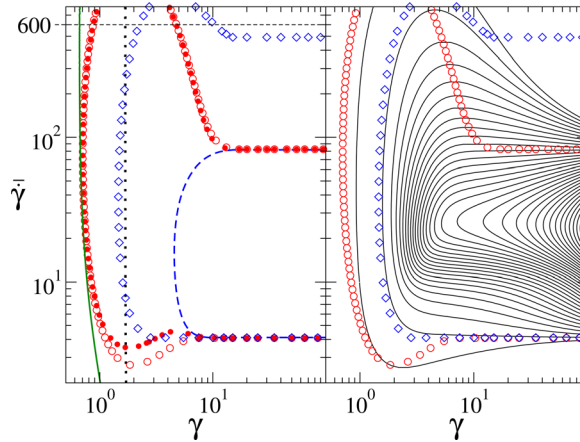
In the left panel of Fig. 15, then, the black dotted line indicates the locus of strain values  $\gamma_0$  for which the base state stress startup curves show a stress overshoot, with these curves measured across a range of closely spaced values of  $\dot{\gamma}_0$ . In other words, in any single startup run corresponding to a horizontal cut across this plane at a fixed  $\dot{\gamma}_0$ , the stress overshoot occurs at the strain indicated by this black dotted line. This line being vertical indicates that, in this version of the rolie poly model without chain stretch, the stress overshoot occurs at a fixed strain  $\gamma \sim 1.7$  for all values of imposed shear rates (Once chain stretch becomes important this is no longer true, see Sec. VII B 2.).

The green solid line indicates the strain at which our criterion (54) for “elastic instability” is first met in each horizontal startup slice. As can be seen this occurs just before overshoot in each run, due to the presence of the stress curvature terms in Eq. (54).

The dashed line encloses the region of viscous instability in which  $\partial \dot{\gamma} \Sigma_0|_{\gamma_0} < 0$ , according to our criterion (52). At the far right hand side of the plane  $\gamma_0 \rightarrow \infty$  this coincides with the region of negative slope in the underlying constitutive curve.

The large open circles enclose the region in which the full criterion (51) for linear instability to banding is met. We have cross-checked numerically that this indeed coincides with the region in which there exists a positive eigenvalue of the linearised equations, thereby verifying our analytical derivation of Eq. (51).

As can be seen, the full criterion (51) is very well represented by the much simpler elastic one (54) across a wide range of shear rates during the early stage of shear startup towards the left hand side of the  $\dot{\gamma}_0, \gamma_0$  plane, and by the even simpler viscous one (52) at the far right hand side. This ability of the “elastic” and “viscous” criteria separately to capture the full criterion in these regimes leads us further to indicate by the small full circles the region in which a criterion formed simply by summing the elastic terms (54) and the viscous terms (52) is met



**FIG. 15.** Shear startup in the nRP model with a non-monotonic constitutive curve  $\beta = 0.4$ ,  $\eta = 10^{-4}$ . Left panel, black dotted line: location of stress overshoot. Solid line: location of onset of “elastic instability” [Eq. (54)]. Dashed line encloses region of “viscous instability” [Eq. (52)]. Large open circles enclose region of linear instability according to full criterion [Eq. (51)]. Small closed circles enclose region of linear instability according to the criterion with cross terms omitted [Eq. (55)]. Diamonds enclose region in which significant shear banding is seen in our spatially aware nonlinear simulations. Right panel, solid lines: contour lines of equal  $|\delta \dot{\gamma}_{n=1}|/\dot{\gamma} = 10^M$  for integer  $M$  found by directly integrating the linearised Eq. (47) (first contour:  $M = -2$  and we show only contours  $M \geq -2$ ). Circles and diamonds as in left panel.



$$\partial_{\dot{\gamma}_0} \Sigma_0|_{\dot{\gamma}_0} - \frac{1}{\dot{\gamma}_0^2} \text{tr} \mathbf{M} \partial_{\dot{\gamma}_0} \Sigma_0|_{\dot{\gamma}_0} + \frac{1}{\dot{\gamma}_0} \partial_{\dot{\gamma}_0}^2 \Sigma_0|_{\dot{\gamma}_0} < 0. \quad (55)$$

This simple criterion performs well in capturing the region of instability across the full plane of  $(\dot{\gamma}_0, \dot{\gamma}_0)$ , apart a small region at the bottom left.

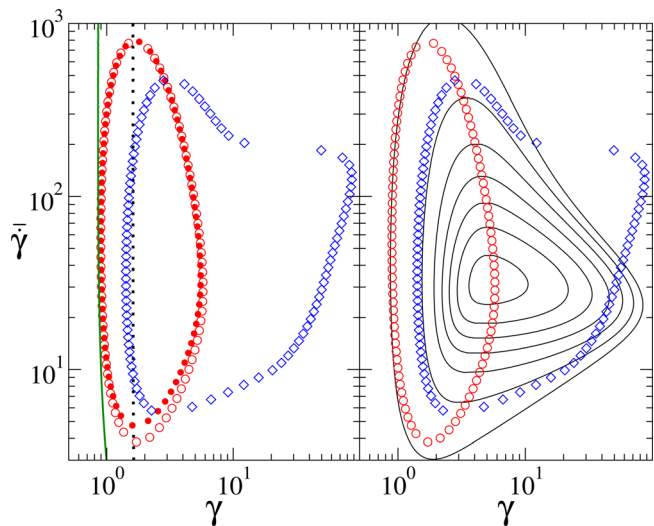
As just described, the left panel of Fig. 15 concerns our criteria for the onset of a positive eigenvalue of the linearised system of Eq. (47), which we propose indicates the onset of a linear instability to shear banding as the underlying homogeneous base state evolves in time. However, as noted above, the concept of a time-dependent eigenvalue should be treated with some caution. Therefore in the right hand panel of Fig. 15 we show results obtained by integrating the linearised Eq. (47) directly. The solid lines are contours of equal  $|\delta \dot{\gamma}_{n=1}|$ , obtained by this process of integration. As can be seen the region of growth and decay in this heterogeneous perturbation agrees well with the eigenvalue-based criteria in the left subpanel, confirming that our concept of a time-dependent eigenvalue is indeed useful.

We also summarise in Fig. 15 the results of a series of fully nonlinear spatially aware simulations of shear startup, performed for a wide range of values of  $\dot{\gamma}$  at closely spaced intervals. Again, any horizontal slice across this plane corresponds to one of these runs at a given  $\dot{\gamma}_0$ . The diamonds show the region of this plane of strain-rate and strain for which significant shear banding is observed (We choose  $\Delta \dot{\gamma} > 0.05 \dot{\gamma}$  as a criterion for significant banding.). As can be seen, the region of significant banding agrees well with expectations based on the linear calculation alone in most regions of the plane. However a window of shear rates either side of the regime of viscous linear instability deserves further comment. Here the nonlinear simulations remain significantly banded in steady state, even though the linear system has returned to stability by then. For such shear rates, a state of homogeneous shear on the underlying constitutive curve is indeed linearly stable, but in fact only metastable: the true steady state is banded. At very high shear rates, e.g.,  $\dot{\gamma} = 600$ , we observe shear bands that form transiently in startup, triggered by the “elastic” instability, but that return to homogeneous flow in steady state (Eventually at extremely high shear rates, once  $\eta \dot{\gamma} > G$ , we see a return to stability conferred by the trivial Newtonian solvent, but we do not expect the model to be valid for such extremely fast flows.).

In summary, the overall stability portrait of the nRP model with a non-monotonic constitutive curve comprises, in this plane of strain-rate and strain, a vertical patch of “elastic instability” at the left side of the plane, and a horizontal patch of “viscous instability” at the right hand side. In between these limits there is a continuous cross-over between the two instabilities.

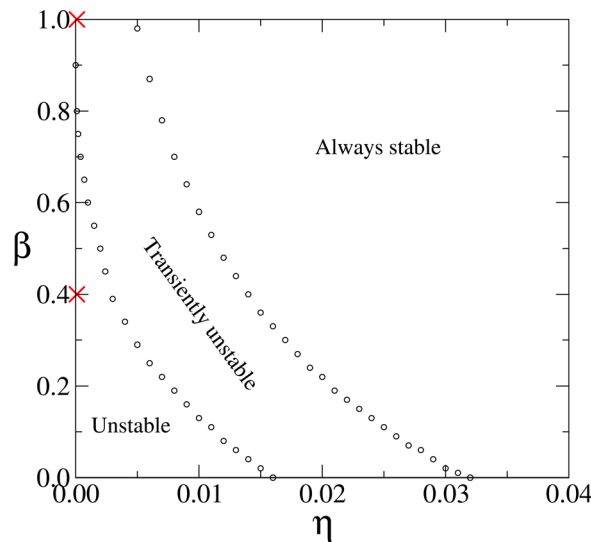
In contrast, for model parameters for which the constitutive curve is monotonic, the patch of “viscous instability” is absent and the eventual steady flowing state is homogeneous at all strain-rates. Importantly, however, a patch of “elastic instability” remains with onset at a strain  $\gamma \approx 1$ , again closely associated with the startup stress overshoot at strain  $\gamma \approx 1.7$  (see Fig. 16). This triggers pronounced shear banding during startup, which however persists only transiently, decaying at larger strains to leave homogeneous flow in steady state. A single startup run corresponding to a horizontal slice across this plane at  $\dot{\gamma}_0 = 30.0$  is explored in 14 (top row). In steady state, the flow is homogeneous with a stress value indicated by the upper cross in Fig. 13.

As can be seen from Fig. 16, the transient bands are predicted to persist for  $O(10-100)$  strain units, depending on the value of the applied shear rate. This is broadly consistent with experimental phenomenology [see, for example, Fig. 4 of Hu *et al.* (2007)].



**FIG. 16.** As in Fig. 15 but now for nRP model with a monotonic constitutive curve,  $\beta = 1.0$ . The “viscous instability” is absent in this case, but the “elastic instability” remains.

So far, we have explored in detail one set of model parameters  $(\beta, \eta) = (0.4, 10^{-4})$  for which the underlying constitutive curve is non-monotonic and a viscous instability persists to steady state; and one set of parameters  $(\beta, \eta) = (1.0, 10^{-4})$  for which the constitutive curve is monotonic and shear bands form only transiently. Denoting these two distinct cases by “unstable” and “transiently unstable,” respectively, we summarise the model’s behaviour in the full plane of  $(\beta, \eta)$  in Fig. 17.



**FIG. 17.** Summary of the linear stability properties of the nRP model as a function of the model parameters  $\beta, \eta$ , during shear startup at a shear rate in the region of minimum slope of the constitutive curve. *Unstable*: linearly unstable to shear heterogeneity at steady state. *Transiently unstable*: system shows linear instability at some time during shear startup but returns to linearly stable at steady state. *Always stable*: the system is always linearly stable to shear heterogeneity. Crosses “ $\times$ ” at  $\beta = 1, 0.4$  at  $\eta = 10^{-4}$  indicate the two sets of parameter values explored in detail in the text.

## 2. Stretching RP model

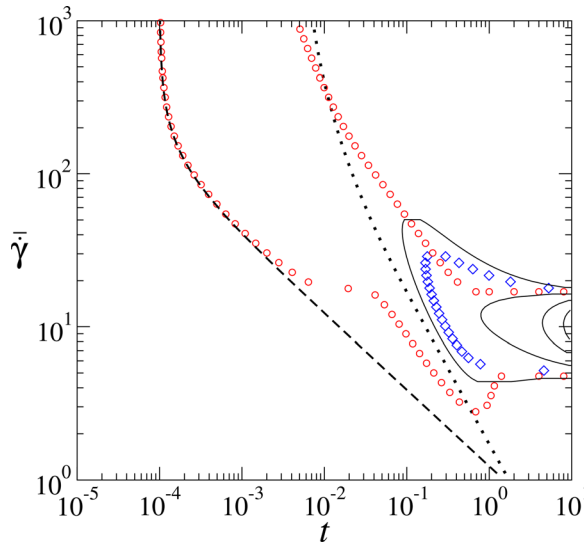
In Subsection VII B 1, we discussed the predictions of the nRP model, in which any possibility of chain stretch is switched off by setting  $\tau_R = 0$ . Recall Eq. (14). We now turn to the sRP model in which chain stretch is accounted for. Recall Eq. (13).

For applied strain-rates  $\dot{\gamma} \ll \tau_R^{-1}$ , no appreciable stretch arises even in the sRP model, and the nRP results discussed above apply directly. This can be seen in Fig. 18: the dynamics in the regime  $\dot{\gamma} \ll \tau_R^{-1}$  is the same as discussed above for the nRP model.

The focus in this section is therefore on shear startup runs performed at shear rates  $\dot{\gamma} > \tau_R^{-1}$ , for which appreciable chain stretch does develop. Here the system exhibits an early-time ( $t < \tau_R$ ) stress-strain behaviour corresponding to that of a linear elastic solid, with  $\Sigma = G\gamma$ . At longer times  $t > \tau_R$  the relaxation of chain stretch leads to deviation from this linear relation and a stress signal that decreases with strain, after an overshoot. In contrast to the nRP model, in which stress overshoot occurs at a fixed value of the strain, in the stretching regime this overshoot now occurs at a fixed time  $t \sim \tau_R$ . Accordingly, the stress startup curve no longer converges to a limiting function of strain  $\Sigma = \Sigma(\gamma)$  at high shear rates, and the concept of a purely “elastic instability” no longer applies. As can be seen in Fig. 18 the onset of an elastic instability just before overshoot is apparent only in the non-stretch regime  $\dot{\gamma} \ll \tau_R^{-1}$  explored previously in the nRP model and breaks down for  $\dot{\gamma} > \tau_R^{-1}$ .

Surprisingly, however, we find a new linear instability, specific to the stretching regime  $\dot{\gamma}_0 > \tau_R^{-1}$ , that sets in at a time *before* overshoot given by

$$t_s = \frac{3}{2\tau_d \dot{\gamma}_0^2} + \eta/G \quad \text{for } \dot{\gamma}_0 \gg \tau_R^{-1}. \quad (56)$$



**FIG. 18.** Stability portrait of the sRP model in the plane of strain-rate and strain for model parameter values  $\beta = 0.4$ ,  $\eta = 10^{-4}$ ,  $\tau_R = 10^{-2}$ ,  $q = 5 \times 10^{-3}$ . Solid lines show contours of equal  $|\delta \dot{\gamma}_n| = \dot{\gamma} 10^M$  for integer  $M$  found by directly integrating the linearised Eq. (47) (The contour nearest  $\partial_t \Sigma = 0$  has  $M = -2$ , and we show only contours  $M \geq -2$ ). Diamonds show the region of significant banding in a full nonlinear spatially aware simulation. For shear rates in the non-stretching regime  $\tau_d^{-1} \ll \dot{\gamma} \ll \tau_R^{-1}$  we recover the behaviour discussed previously in the nRP model. In contrast a “sRP-specific” instability is seen in upper-left region of the plane with onset given by the formula in Eq. (56), which is shown by a dashed line. However it does not precipitate significant banding.

However this instability disappears again even before the overshoot occurs and never leads to observable banding, so we pursue it no further here.

### 3. Rolie-poly model: Relation to shear startup experiments

We have shown that the RP model shows rich time-dependent banding dynamics during shear startup in the nonstretching regime  $\tau_d^{-1} \ll \dot{\gamma} \ll \tau_R^{-1}$ . These results, together with those of Adams *et al.* [Adams *et al.* (2011); Adams and Olmsted (2009a, 2009b)], demonstrate that the RP model captures the experimental phenomenology of entangled polymeric fluids in this shear startup protocol. We summarise this now, divided into three classes (i)–(iii) for convenience.

(i) For imposed shear rates in the negatively sloping regime of a non-monotonic underlying constitutive curve, we find shear banding that sets in around the time of an overshoot in the stress startup curve and is initially sufficiently violent as to lead to elastic recoil and negative local shear rates or velocities. It persists to steady state but with much smaller magnitude than around the time of overshoot. This is consistent with experimental observations of Ravindranath *et al.* (2008), Ravindranath and Wang (2008), Boukany and Wang (2009a), Tapadia and Wang (2006), and Boukany and Wang (2009c). (ii) For imposed shear rates some distance above the negatively sloping regime of a non-monotonic constitutive curve, we again find violent shear banding setting in around the time of stress overshoot during startup. However these bands persist only transiently, and decay to leave a homogeneous steady state. This is consistent with experimental observations of Boukany and Wang (2009a) and Ravindranath *et al.* (2008). (iii) For a monotonic constitutive curve we again see pronounced transient banding triggered by stress overshoot, which decays to leave a homogeneous steady state, as in experimental observations of Hu *et al.* (2007), Ravindranath *et al.* (2008), and Boukany and Wang (2009a).

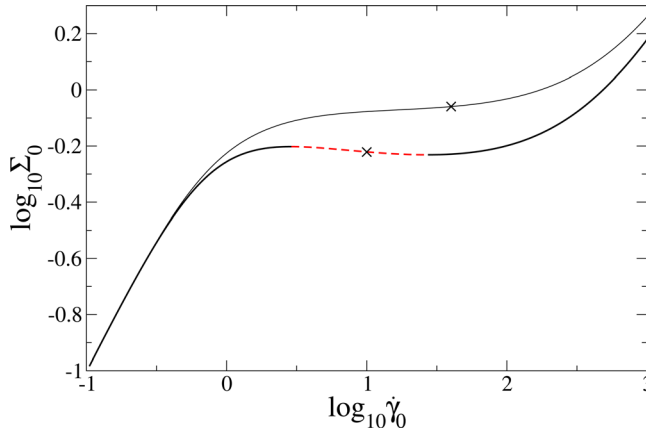
The main new contribution of the present manuscript has been to place these observations in the context of our general analytical criterion for the onset of banding.

### C. Numerical results: Giesekus model

We now discuss our numerical results for shear startup in the Giesekus model. Our aim is to address whether this model is capable of capturing the time-dependent shear banding behaviour observed experimentally in entangled polymers, summarised in (i)–(iii) above. To provide a fair comparison with the RP model, we choose values of the parameter  $\alpha$  giving constitutive curves that are as closely comparable between the models as possible. Compare Fig. 19 with Fig. 14.

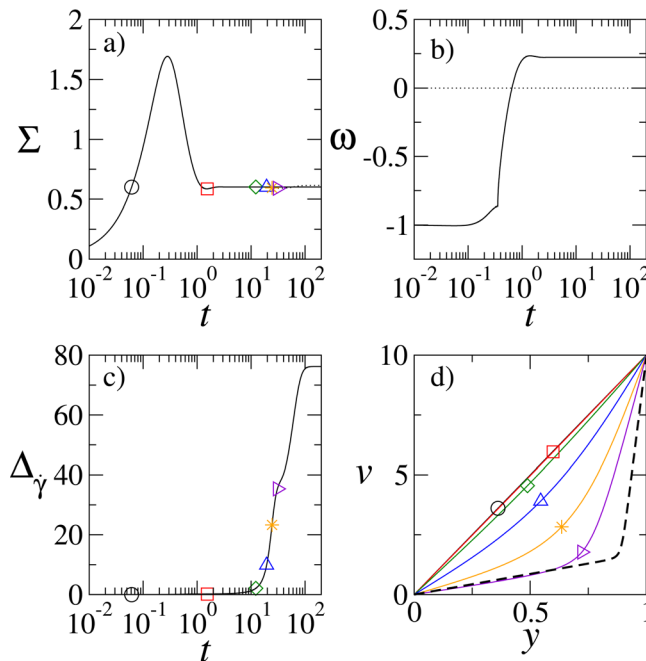
To explore class (i) behaviour, we consider the non-monotonic constitutive curve of Fig. 19 and perform a shear startup at a value of the shear rate represented by the cross in the negatively sloping regime (see Fig. 20). The stress startup curve closely resembles that of the RP model, with a pronounced overshoot. However the Giesekus model apparently lacks the region of pronounced elastic instability associated with this overshoot. Instead, the degree of banding  $\Delta\dot{\gamma}$  rises monotonically and only becomes significant at long times, when the criterion  $\partial\dot{\gamma}\Sigma|_{\dot{\gamma}\rightarrow\infty} < 0$  for viscous instability and steady state banding is met. For shear rates outside the negatively sloping regime of this constitutive curve (not shown), we find no banding during startup or in steady state. The Giesekus model therefore fails to address classes (i) and (ii) of polymeric startup behaviour described above.

To explore class (iii) behaviour, we consider the monotonic constitutive curve of Fig. 19 and perform a shear startup at a value of the shear rate represented by the cross in the region of weakest slope (see Fig. 21). The stress startup curve again closely resembles

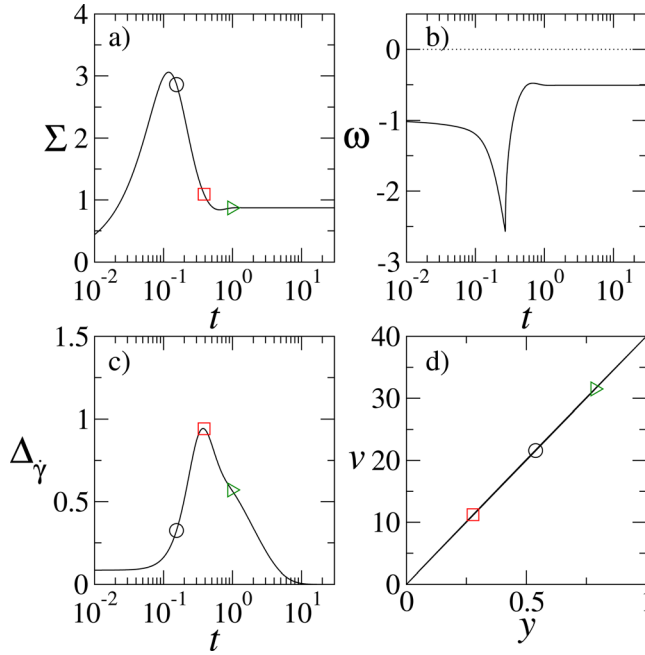


**FIG. 19.** Constitutive curves for the Giesekus model with  $\alpha = 0.6, 0.8$  (top to bottom) and  $\eta = 10^{-3}$ . Regime of linear instability is shown as a dashed line. Crosses indicate shear rates  $\dot{\gamma} = 10, 40$  for which time-dependent behaviour is shown in Figs. 20 and 21, respectively.

that of the RP model. However the magnitude of transient shear banding is significantly diminished in comparison, never exceeding 10% of the overall imposed shear rate  $\dot{\gamma}$ . Indeed, no eigenvalue shows a positive real part during startup for a monotonic constitutive curve in this model. Accordingly, the Giesekus model lacks the pronounced “elastic instability” of the RP model and fails to address class (iii) behaviour also.



**FIG. 20.** Shear startup in Giesekus model at an applied shear rate  $\dot{\gamma} = 10$  in the negative sloping regime of the non-monotonic constitutive curve of Fig. 19 with  $\alpha = 0.8$ ,  $\eta = 10^{-3}$ . (a) Shear stress startup curve (results with heterogeneity allowed are indistinguishable from the homogeneously constrained system). (b) Largest real part of any eigenvalue from linear stability analysis  $\omega$ . (c) Degree of banding in the nonlinear simulation,  $\Delta\dot{\gamma} = \dot{\gamma}_{\max} - \dot{\gamma}_{\min}$ . (d) Snapshots of the velocity profile in the nonlinear simulation at strains corresponding to symbols in (a), (c). The steady state velocity profile is shown as a thick, dashed line. Magnitude of initial noise  $q = 10^{-2}$ .



**FIG. 21.** As in Fig. 20, but now for an applied shear rate  $\bar{\dot{\gamma}} = 40$  at the weakest slope of the constitutive curve of Fig. 19 with  $\alpha = 0.6$ ,  $\eta = 10^{-3}$  Z,  $\alpha = 0.6$ ,  $\eta = 10^{-3}$ .

A thorough exploration of this parameter space  $\alpha, \eta, \bar{\dot{\gamma}}$  (not shown) confirms that the above comments of negligible banding during startup apply generically in the Giesekus model. This obviously contrasts sharply with our results for the RP model above. The reason for this appears to be the different structure of the loading terms between the Giesekus and RP models [compare Eq. (15) with Eq. (14)]. Because of this difference, the Giesekus model does not attain a limiting nonlinear shear startup curve  $\Sigma(\dot{\gamma})$  at high shear rates, and accordingly lacks the possibility of an elastic instability.

## VIII. CONCLUSIONS AND OUTLOOK

We have explored theoretically the onset of shear banding in polymeric and wormlike micellar fluids for three of the most common time-dependent rheological protocols: step stress, strain ramp, and shear startup. For each protocol we have developed a fluid-universal criterion for the onset of linear instability to shear banding. We have supported these predictions with numerical simulations of the rolie-poly and Giesekus models. Between these models, we have found the rolie-poly model to be effective in capturing the observed experimental phenomenology. In contrast, the Giesekus model apparently fails to do so.

Following the imposition of a step stress, a base state of initially homogeneous creep response becomes unstable to the formation of shear bands during any regime in which the shear rate  $\dot{\gamma}(t)$  is simultaneously upwardly curving and upwardly sloping in time  $\partial_t^2 \dot{\gamma} / \partial_t \dot{\gamma} > 0$ . We believe this criterion to be universal in all models for the rheology of complex fluids of which we are aware. We showed that such a regime does indeed arise in both the Giesekus and RP models for imposed stresses nearest those on the weakest slope of the underlying constitutive curve of shear stress as a function of shear rate.

However the magnitude of the resulting shear banding only attains a magnitude consistent with experimental findings [Ravindranath and Wang (2008); Tapadia and Wang (2003); Hu *et al.* (2008); Boukany and Wang (2008); Hu and Lips (2005); Boukany and Wang (2009c)] in the RP model.

For the strain ramp protocol, a base state of initially homogeneous shear response is left unstable immediately post-ramp if the stress had been decreasing with strain towards the end of the ramp. We believe this criterion to be general for all ramps applied at a rate exceeding the inverse of the material's intrinsic relaxation time, for any viscoelastic constitutive equation that can be expressed as the sum of separate loading and relaxation terms.

In the RP model, we demonstrated numerically that this criterion for instability immediately post-ramp is met for ramp rates in the nonstretching regime  $\tau_d^{-1} \ll \dot{\gamma}_0 \ll \tau_R^{-1}$ , and ramp amplitudes  $\gamma_0 \gtrsim 1.7$ . However we further explored the RP model's full relaxation as a function of the time elapsed since the ramp ended, following ramps that are either slow or fast relative to the rate of chain stretch relaxation  $\tau_R^{-1}$ . In the absence of CCR, the stress relaxation function of a "fast" ramp drops onto that of a "slow" ramp once chain stretch has relaxed. This leads to a delayed shear banding instability following a "fast" ramp, even though in that case the stress increased monotonically with strain during the ramp. In contrast CCR tends to stabilise the system against this "delayed" banding instability. In capturing such rich phenomenology, we again find the RP model capable of addressing the experimental data for polymeric fluids, while the Giesekus model would be expected to perform poorly in comparison.

Finally we explored the onset of shear banding in the shear startup protocol. For materials that attain a limiting nonlinear startup curve of stress as a function of strain at high strain-rates, we identified separate "elastic" and "viscous" instabilities that respectively act at early and late times during startup. We confirmed the presence of these two distinct regimes in a numerical study of the RP model, which shows a violent elastic instability at early times during startup at rates  $\tau_d^{-1} \ll \dot{\gamma} \ll \tau_R^{-1}$ , closely associated with an overshoot in the stress startup signal. This banding persists to steady state in any regime of negative slope in the underlying constitutive curve (i.e., of viscous instability), but with a "degree of banding" that is much weaker than that seen during the initial elastic instability. In contrast the Giesekus model does not attain a limiting startup curve of stress as a function of strain at high strain-rates and lacks a violent elastic instability during startup, in contrast to experimental observations. It does, however, correctly capture steady state banding. Accordingly we conclude that the RP model provides a good description of shear banding during time-dependent flows in entangled polymeric fluids, while the Giesekus model performs poorly in comparison.

Throughout the manuscript we have assumed the condition of no-slip at the wall of the flow cell. However slip is observed almost ubiquitously in experiments on shear banding fluids. It remains an important open challenge for theorists to develop models for the rheology of the layer of fluid adjacent to the wall of the flow cell, of the same microscopically sound status as (for example) the rolie-poly model used here for the bulk fluid, and to use these to examine the interplay of wall effects with bulk banding phenomena.

Our results in the RP and Giesekus models have, for the purpose of distilling the origin of shear banding behaviour, been limited to a single-mode description of entangled polymeric materials. In practice it is common to use a multi-mode approach; further work is needed to ascertain whether the shear banding properties outlined here persist in such a multi-mode description.

The fluid-universal criteria that we have derived here (and discussed in the context of polymer fluids) will be explored in the context of a broad class of disordered soft glassy materials including foams, dense emulsions and colloids in a future publication.



## ADDENDUM

Since this article was submitted a manuscript has been published [Li *et al.* (2013)] describing new experiments that did not find shear banding in shear startup or step strain in polymer solutions. Further work is clearly needed to reconcile the experimental observations and theoretical predictions discussed in this manuscript with that new experimental contribution.

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